

**Pressure-induced phase transitions in liquid crystals: A molecular field approach**Sudeshna DasGupta,<sup>1,\*</sup> Sabana Shabnam,<sup>1,†</sup> Soumyajit Pramanick,<sup>1,‡</sup> Nababrata Ghoshal,<sup>2,§</sup>  
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(Received 11 February 2018; revised manuscript received 16 July 2018; published 1 August 2018)

A rigorous microscopic treatment of a nematic fluid system based on a pairwise interaction potential is immensely complex. For studying such systems molecular field theories are often the standard method of choice. In this paper we have chosen a simple effective potential  $U = \frac{u_4}{v^4} - \frac{u_2}{v^2} - \frac{Au_2}{v^2} \langle P_2 \rangle P_2(\cos \vartheta)$  to study an isothermal-isobaric ensemble describing a liquid crystalline system. Using this we have studied in particular the pressure dependence of liquid crystalline phase transitions.

DOI: [10.1103/PhysRevE.98.022701](https://doi.org/10.1103/PhysRevE.98.022701)**I. INTRODUCTION**

Studies of phase transitions in liquid crystalline materials are of extreme importance because of their various important applications. For more than a century different experiments and corresponding theoretical studies have established the existence and behavior of different liquid crystalline phases. These studies involve the measurement of variation of different liquid crystalline properties such as orientational order parameter, dielectric constant, specific heat, isothermal compressibility, isobaric expansivity, etc. with the temperature [1–3]. Most of these thermodynamic measurements have been done on nematics at constant pressure, so that as temperature is varied, the molar volume also varies as a result of thermal expansion. The temperature dependence of orientational order in a nematic liquid crystal at constant molar volume was difficult to measure. This was first carried out by McColl and Shih [4]. They published their results of the temperature and volume variation of the orientational order parameter in para-azoxyanisole (PAA).

One of the first experiments investigating the effect of pressure on mesophase transitions were conducted by Hulett in 1899 [5] just about a decade after the discovery of liquid crystals. Most of the work involving pressure dependence had been done during 1970s [4,6–9]. Then in 1975, Shashidhar and Chandrashekar [6] in their experimental work presented the pressure variation of liquid crystalline materials in detail and generated the phase diagrams, which clearly showed the liquid crystalline phases and the appearance of tricritical points. Horn [2,3], on the other hand, determined the dependence of orientational order parameter with temperature by measuring

refractive index. Later Horn along with Faber explained these experimental data using a mean-field approach [7]. Wallis and Roy [8] again by the proton NMR spectrum study, studied the line width of proton resonance as function of temperature and pressure for the nematogens 5, 6, 7, and 8 CB and also for some other nematogens including PAA. They showed that the value of the orientational order parameter at the nematic-isotropic transition decreases with increasing pressure for 5, 7, and 8 CB but remained constant for 6 CB. The pressure and temperature dependence of the orientational order parameter for different sites in a mesogen were reported by Emsley *et al.* [9]. They showed that the quadrupolar splitting at the nematic isotropic transition temperatures is independent of pressure for different sites of the alkyl chain. In 1980, Luckhurst and Romano [10] considered an anisotropic part of the intermolecular potential along with the isotropic part and carried out computer simulation studies to find the phase diagram for some liquid crystals, but they had not considered any variation in pressure. In 1999, Hess and Su [11] used a generalization of the Lennard-Jones potential to study both the pressure and temperature variation of their liquid crystal model with density and observed a pseudotricritical point.

The stability of the nematic liquid crystal phase arises from the existence of strong interactions between pairs of the constituent molecules. This interaction between molecules leads to a long-range orientational order in the nematic phase. In most realistic situations, a rigorous microscopic treatment of a nematic fluid system based on a pairwise interaction potential becomes immensely complex. For systems of comparable complexity, mean-field theories are often the standard method of choice. The celebrated Maier-Saupe molecular field theory [12] (also referred to as mean-field theory; for a clarification of the terminology being used here see Ref. [13]) of nematic liquid crystals correctly predicts the existence of a first-order phase transition between the nematic and isotropic liquid states. However, there has been no significant molecular field study of the pressure dependence of liquid crystalline phase transitions to date. In the present paper we have presented a

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molecular field calculation based on a very simple model for an isothermal-isobaric (NPT) liquid crystalline system, with the specific aim of exploring this facet of the topic. With the advent of modern-day computing the problem of interacting systems can often be tackled by using various computational methods. We feel, however, that models such as ours, which rely on simple physical principles, have their own role to play especially in elucidating the physical features of a system.

## II. OUR MODEL

Hard rod models, which mimic a nematic liquid crystalline system are very sensitive to variations of density. This variation can be studied best using the isothermal-isobaric ensemble, denoted as the NPT ensemble. Any realistic theoretical model of nematics must include both repulsive and attractive interactions [14] as both the anisotropic attractions and steric repulsions have equally important effects in nematics. Keeping this in mind, in this paper we have modified the Maier-Saupe potential energy [15] given by

$$U_{MS} = -\frac{A}{v^2} \langle P_2 \rangle P_2(\cos \vartheta) \quad (1)$$

to include an isotropic volume-dependent term and have studied a liquid crystalline material using a molecular field approach. The effective single-particle potential we choose for this purpose is given by

$$U = \frac{u_4}{v^4} - \frac{u_2}{v^2} - \frac{Au_2}{v^2} \langle P_2 \rangle P_2(\cos \vartheta), \quad (2)$$

where  $u_4$ ,  $u_2$ , and  $A$  are constants and  $v$  is the volume of the fluid per molecule. Here the volume dependence of the isotropic term has been chosen to mimic the scaling behavior of the familiar Lennard-Jones potential. The attractive term  $-\frac{u_2}{v^2}$  serves to ensure that the molecules do not move too far apart to form a liquid, while the repulsive term  $\frac{u_4}{v^4}$  ensures that the molecules do not collapse to zero volume under the attraction.  $A$  is a phenomenological constant that expresses the relative strength of the anisotropic interaction in comparison to the attractive part of the isotropic term. Note that this is similar to the kind of approach described in Ref. [15] that was used by Maier and Saupe to arrive at the molecular field potential [Eq. (1)]. It should be noted that this is a very simplified model of a nematic liquid crystal, which ignores the departure of real molecules from uniaxiality and does not take into account the fact that real molecules are flexible. In spite of these over simplifications the final results match predicted values reasonably well, at least qualitatively.

The need for the isotropic part of the potential is not difficult to see. In the canonical ensemble, the system is at a fixed volume and although the strength of the anisotropic potential as described by [Eq. (1)] has a volume dependence, the strength  $\frac{A}{v^2}$  is effectively a constant. However, in the isothermal-isobaric ensemble we allow the volume of the system to fluctuate. In the absence of a term such as  $\frac{u_4}{v^4}$  that penalizes very small volumes (and hence very small intermolecular distances) the system would have tended to zero volume in equilibrium, a result that is obviously absurd. Again, it may seem that the attractive term  $-\frac{u_2}{v^2}$  is unnecessary because of a similar behavior of the anisotropic term. However, note that the anisotropic term is not

uniformly attractive; it may also be repulsive depending on the sign of  $P_2(\cos \theta)$  and this term alone leads to equilibrium mean molecular separations that are too large for the formation of liquid phases.

Using this potential the canonical partition function can be written as

$$Z_{NVT} = \frac{V^N}{N! \Lambda^{3N}} (Z_1 \exp(\beta \langle U \rangle))^N \exp \left[ -N\beta \left( \frac{u_4}{v^4} - \frac{u_2}{v^2} \right) \right], \quad (3)$$

where

$$Z_1 = \exp \left( -\frac{\beta}{2} \left( \frac{u_4}{v^4} - \frac{u_2}{v^2} \right) \right) \int_0^1 \exp \left( \frac{\beta Au_2}{v^2} \langle P_2 \rangle P_2(\cos \vartheta) d(\cos \vartheta) \right) \quad (4)$$

is the single-molecule partition function,  $\beta = 1/k_B T$  and  $V$  is the volume of the system.

Hence the partition function for an isothermal-isobaric ensemble is

$$Z_{NPT} = \int_0^\infty \frac{1}{V_0} \exp(-\beta p V) Z_{NVT} dV, \quad (5)$$

which becomes

$$Z_{NPT} = \frac{N^{N+1}}{N! V_0 \Lambda^{3N}} \int_0^\infty \exp[Nf(v)] dv, \quad (6)$$

where

$$f(v) = -\beta p v + \ln v + \ln Z_1 + \frac{\beta}{2} \langle U \rangle - \frac{\beta}{2} \left( \frac{u_4}{v^4} - \frac{u_2}{v^2} \right). \quad (7)$$

$f(v)$  depends on  $v$  and  $\langle P_2 \rangle$  and on the constant parameters  $p$ ,  $\beta$ ,  $u_2$ ,  $u_4$ , and  $A$ . Here we are singling out its volume dependence since we are going to use the saddle-point method where the integral is only over volume. Since  $N \gg 1$  we can use the saddle-point approximation (see Appendix) to write

$$Z_{NPT} = \frac{N^{N+1}}{N! V_0 \Lambda^{3N}} \exp[Nf(v_*)], \quad (8)$$

where  $v_*$  is the value of  $v$  that maximizes  $f(v)$ .

To maximize  $f(v)$  we differentiate  $f(v)$  with respect to  $v$  and equate it to zero. From  $\frac{\partial f}{\partial v} = 0$  we obtain the equation

$$p - \frac{1}{\beta v_*} - \frac{2u_4}{v_*^5} + \frac{u_2 + Au_2 \langle P_2 \rangle^2}{v_*^3} = 0. \quad (9)$$

Using this  $f(v_*)$  we can construct the Gibb's free energy of the system given by

$$G\beta = -Nf(v_*) - \frac{3N}{2} \ln \beta$$

up to a constant. Hence the Gibb's free energy of the system in units of  $k_B T$  is given by

$$G\beta = N \left( p\beta v_* - \ln v_* + \frac{\beta u_4}{2 v_*^4} - \frac{\beta u_2}{v_*^2} - \ln Z_1(\lambda) + \frac{Au_2 \beta \langle P_2 \rangle^2}{2v_*^2} \right) - \frac{3N}{2} \ln \beta, \quad (10)$$

where  $\lambda = \frac{Au_2 \beta}{v_*^2} \langle P_2 \rangle$ .

Now by minimizing Eq. (10) with respect to  $\langle P_2 \rangle$  we obtain

$$\langle P_2 \rangle = \frac{Z'_1}{Z_1}. \quad (11)$$

Solving Eqs. (9) and (11) simultaneously we obtain the value of  $\langle P_2 \rangle$  and  $v_*$ . Again solving Eq. (9) for  $\langle P_2 \rangle = 0$  yields the value of  $v_*$  for the isotropic phase. Out of these two possibilities the equilibrium value of  $\langle P_2 \rangle$  and  $v_*$  for a particular set of constant parameters  $p, \beta, u_2, u_4$ , and  $A$  is decided by checking which of these yield the lower value of  $G$ . This value of  $v_*$  and  $\langle P_2 \rangle$  globally minimizes the function  $G$ .

Now we obtain the critical constants  $P_c, \beta_c$ , and  $v_c$  for the isotropic-vapor transition from Eq. (9) (setting  $\langle P_2 \rangle = 0$ ) in terms of  $u_2$  and  $u_4$ .

$$\frac{v_c^2}{\beta_c} = \frac{3}{2}u_2 \quad (12)$$

$$v_c^2 = \frac{20u_4}{3u_2} \quad (13)$$

$$\frac{1}{\beta_c} = \frac{9u_2^2}{40u_4} \quad (14)$$

$$P_c \beta_c v_c = \frac{8}{15}. \quad (15)$$

All the results that we will discuss in this paper have been obtained in terms of reduced parameters  $\pi = \frac{p}{p_c}, \omega = \frac{v}{v_c}, \vartheta = \frac{T}{T_c}$ . To compare with experimental data for any particular liquid crystal we will need the critical constants of that substance. As an example we cite that using the value of the critical constants for 8OCB (Octyl-oxycyanobiphenyl),  $p_c = 1.43$  MPa and  $T_c = 1091$  K [16] we have calculated the values of the constants  $u_2 = 19.03 \times 10^{-50}$  and  $u_4 = 8.97 \times 10^{-103}$  in S.I. units, which are of reasonable order in the molar context.

From Eq. (9) we obtain the reduced equation of state

$$\pi = \frac{15\vartheta}{8\omega} + \frac{3}{8\omega^5} - \frac{5}{4\omega^3}(1 + A\langle P_2 \rangle^2). \quad (16)$$

The corresponding free energy in terms of the reduced set of parameters  $\pi, \omega$ , and  $\vartheta$  is

$$G_R = \frac{8\pi\omega}{15\vartheta} - \log \omega + \frac{1}{20\vartheta\omega^4} - \frac{1}{3\vartheta\omega^2} - \log Z_1 \left( \frac{2A\langle P_2 \rangle}{3\vartheta\omega^2} \right) + \frac{A\langle P_2 \rangle^2}{3\vartheta\omega^2} + \frac{3}{2} \log \vartheta. \quad (17)$$

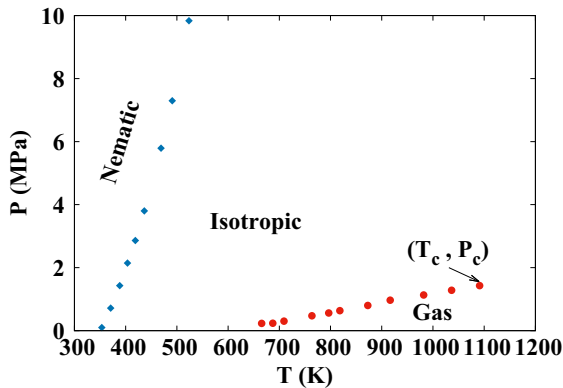


FIG. 1. Phase diagram showing the nematic, isotropic liquid, and gaseous phases.

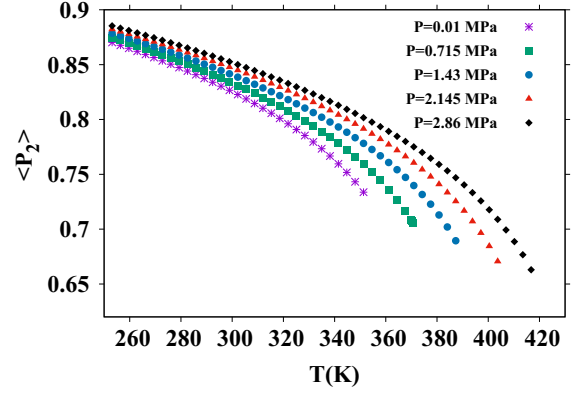


FIG. 2. Variation of orientational order parameter with temperature.

In this paper we have used Eqs. (16) and (17) and obtained the values of  $\langle P_2 \rangle$  and  $\omega$ . Again solving Eq. (16) for  $\langle P_2 \rangle = 0$  yields the value of  $\omega$  for the isotropic phase. Out of these two values the equilibrium value of  $\langle P_2 \rangle$  and  $\omega$  is decided on the basis of which of these two values yields a lower  $G_R$ .

### III. RESULTS AND DISCUSSIONS

Our results have been obtained in terms of reduced pressure, volume, and temperature with  $A$  as a free parameter. For the sake of definiteness, while converting to standard units we have chosen  $p_c = 1.43$  MPa and  $T_c = 1091$  K, which are the critical pressure and critical temperature values for 8OCB, as predicted by the Joback method [16]. We have taken the value of  $A = 0.675$ , which helped us fit these predicted values for 8OCB quite well.

Figure 1 shows the phase diagram obtained by us indicating the nematic, isotropic liquid, and the gaseous phases. We can see that the isotropic liquid-gas transition ends in a critical point. In the phase diagram obtained by us we can see that even at low pressures the system exhibits a nematic phase with the nematic-isotropic phase transition occurring at around 353 K.  $\frac{dT_{NI}}{dP}$  has been calculated from this phase diagram to be 221 K/MPa. Shashidhar and Chandrasekhar in 1975 studied the effect of pressure on phase transitions [6]. On the basis of their experiments they found pressure-induced mesomorphism

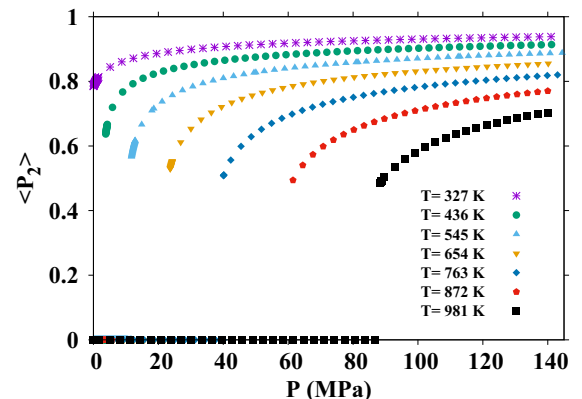


FIG. 3. Variation of orientational order parameter with pressure.

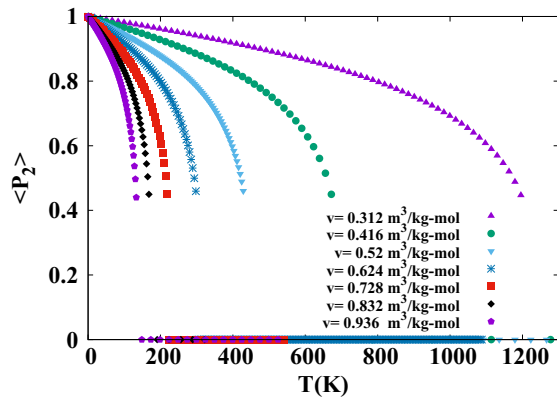


FIG. 4. Orientational order parameter vs  $T$  plot at different constant values of volume.

in methoxy and ethoxybenzoic acids. At atmospheric pressures the compound showed just a single transition, the solid-liquid melting transition. As pressure was raised both compounds showed mesophases. However, propoxybenzoic acid and the higher homologues show at least one liquid crystalline phase at atmospheric pressure [17].

Figure 2 shows the variation of orientational order parameter with temperature for different values of pressure. Here we observe a first-order nematic-isotropic phase transition indicated by a finite discontinuity in the value of the orientational order parameter. The orientational order parameter jumps to zero (for all constant values of pressure) at the transition temperature  $T_{NI}$  (note that the  $Y$  axis of the graph has been truncated to clearly display the different curves). The transition is seen to occur at higher and higher values of temperature with the increase in pressure.

Variation of orientational order parameter with pressure at different values of temperature also shows a first-order nematic-isotropic phase transition as is shown in Fig. 3. The first-order transition is indicated by a finite discontinuity in the value of the orientational order parameter. The transition is seen to occur at higher and higher values of pressure with the increase in temperature. A marginal decrease in the value of the discontinuity with the increase in the value of temperature is observed here.

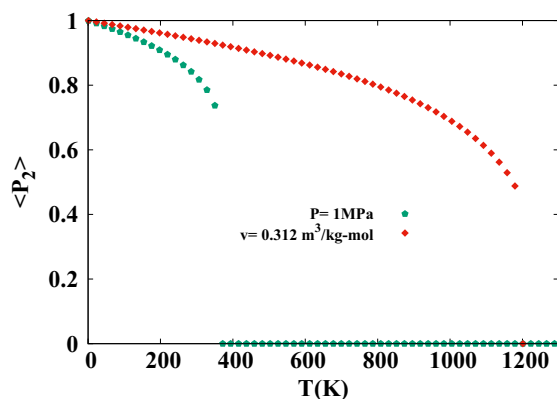


FIG. 5. Comparison of orientational order parameter values at constant volume and constant pressure.

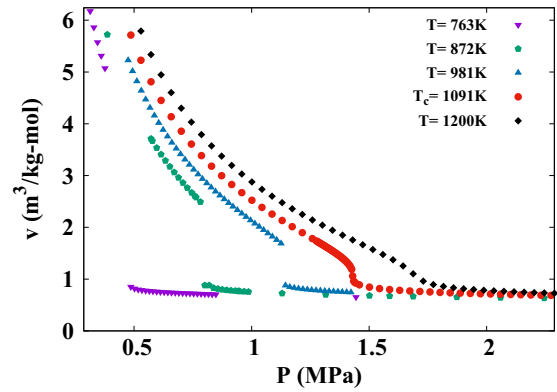


FIG. 6. Variation of volume with pressure for different constant values of temperature showing the isotropic liquid-gas phase transition.

Figure 4 shows the variation of orientational order parameter with temperature at different constant values of volume. The plots indicate that the value of the orientational order parameter at the transition point is nearly independent of pressure as was observed by Horn and Faber [7].

Figure 5 indicates that the thermal range of the nematic phase increases to a huge extent at constant volume as compared to constant pressure. This is consistent with the findings of McColl and Shih who in 1972 [4] had reported experimental studies on PAA, which showed that the thermal range of the nematic phase is increased from 18 K at constant pressure to 47.5 K at constant volume by more than a factor of 2.5.

Figure 6 shows the variation of volume of the system with pressure at different constant values of temperature. The figure shows the isotropic liquid-gas phase transition. It is evident from the plots that the discontinuity in volume gradually decreases with the increase in temperature and at  $T = 1091 \text{ K}$  the discontinuity vanishes indicating the existence of a critical point.

Figure 7 shows the variation of volume of the system with pressure at different constant values of temperature. The figure shows the nematic-isotropic liquid phase transition. From the plots we can see that as temperature increases the discontinuity in volume decreases but even at a very high temperature

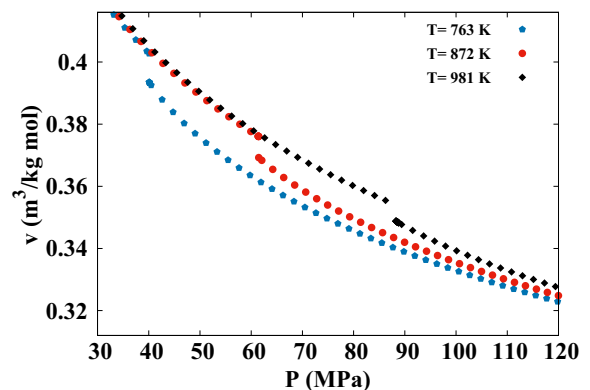


FIG. 7. Variation of volume with pressure for different constant values of temperature showing the first-order nematic-isotropic liquid phase transition.

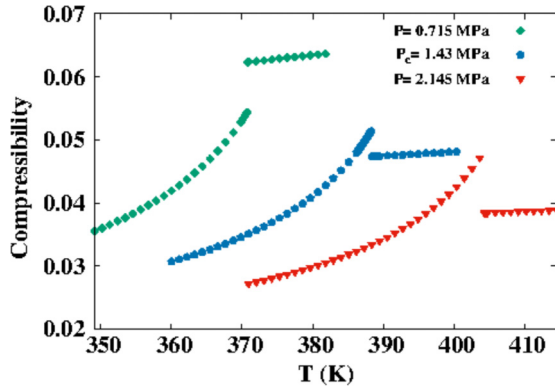


FIG. 8. Variation of isothermal compressibility with temperature showing the nematic-isotropic phase transition.

of around 981 K there is a finite discontinuity showing that the nematic-isotropic phase transition remains a first-order transition throughout.

Figures 8 and 9 show the variation of isothermal compressibility and volume expansivity respectively with temperature near the nematic-isotropic phase transition for three different pressures (below, above and at the critical point). From the curves we can see that at the critical pressure  $P_c = 1.43$  MPa both the compressibility as well as expansivity diverges at around 388 K showing a nematic-isotropic phase transition.

Figures 10 and 11 show the variation of isothermal compressibility and volume expansivity, respectively, with temperature near the isotropic liquid-vapor phase transition for three different pressures (below, above and at the critical point). From the curves we can see that at the critical pressure  $P_c = 1.43$  MPa both the compressibility as well as volume expansivity diverges at around 1100 K denoting the isotropic liquid-vapor phase transition.

#### IV. CONCLUSIONS

We note that the simple model potential that we have introduced reproduces the known behavior of nematic systems as far as the dependence of the transition on pressure is concerned. Given the simplicity of the model, this qualitative agreement gives us confidence in the basic soundness of

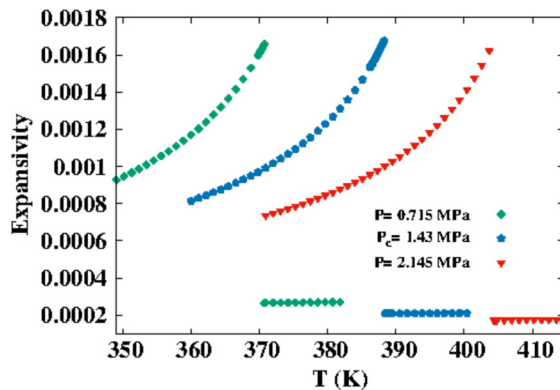


FIG. 9. Variation of volume expansivity with temperature showing the nematic-isotropic phase transition.

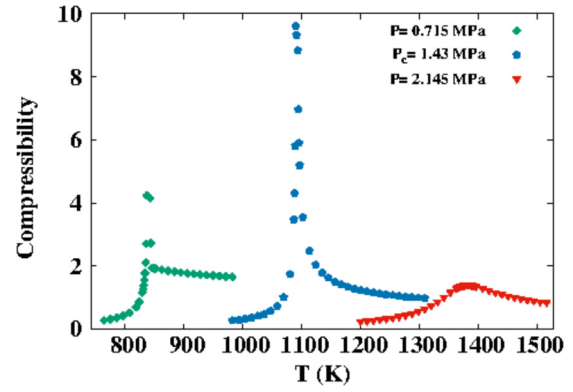


FIG. 10. Variation of isothermal compressibility with temperature showing the isotropic liquid-vapor phase transition.

the underlying physical assumptions. As we have used here the procedure involves only one adjustable parameter  $A$ . We have also used the critical parameters  $T_c, p_c$  of the isotropic-vapor transition of the material as input. As most of the known nematics decompose before reaching critical point, the latter values are usually available only in the form of model-dependent estimates. We can adjust these as well to get a better quantitative fit with experimental data.

#### ACKNOWLEDGMENT

S.S. and S.P. are thankful to DST INSPIRE and UGC, respectively, for support from their fellowships.

#### APPENDIX: SADDLE-POINT APPROXIMATION

Because of the very large value of  $N$ , the integral  $\int e^{Nf(v)} dv$  is completely dominated by the peak value of  $f(v)$  at  $v_*$ . Changing variables to

$$v = v_* + \frac{\delta}{\sqrt{N}}$$

we get

$$Nf(v) = Nf(v_*) + \frac{1}{2} f''(v_*) \delta^2 + \frac{1}{3! \sqrt{N}} f'''(v_*) \delta^3 + \dots$$

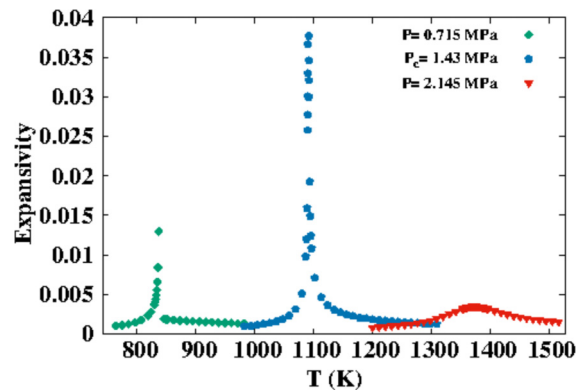


FIG. 11. Variation of volume expansivity with temperature showing the isotropic liquid-vapor phase transition.



so that

$$e^{Nf(v)} = e^{Nf(v_*)} e^{\delta^2 f''(v_*)/2} \left( 1 + \frac{f'''(v_*)}{6\sqrt{N}} \delta^3 + \dots \right)$$

and hence

$$\int e^{Nf(v)} dv = e^{Nf(v_*)} \int e^{\delta^2 f''(v_*)/2} \left( 1 + \frac{f'''(v_*)}{6\sqrt{N}} \delta^3 + \dots \right) \frac{d\delta}{\sqrt{N}}.$$

It is easy to see that this yields

$$\ln \left( \int e^{Nf(v)} dv \right) \approx Nf(v_*) + \ln \left( \sqrt{\frac{2\pi}{N|f'''(v_*)|}} \right) + \dots.$$

Note that for very large values of  $N$ , the subleading term in the above expression, which is of order  $\ln N$  is completely dominated by the leading term of order  $N$  so that we can use

$$\ln \left( \int e^{Nf(v)} dv \right) \approx Nf(v_*).$$

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