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Sabana Shabnam, Sudeshna DasGupta, Nababrata Ghoshal, Ananda DasGupta, and Soumen Kumar Roy

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Sabana Shabnam,[1,a)] Sudeshna DasGupta,[2,b)] Nababrata Ghoshal,[3,c)] Ananda DasGupta,[4,d)] and Soumen Kumar Roy[5,e)]

AFFILIATIONS

[1]School of Physical Sciences, National Institute of Science Education and Research, HBNI, P.O. Jatni, Odisha 752050, India
[2]Department of Physics, Lady Brabourne College, Kolkata 700017, India
[3]Department of Physics, Ramsaday College, Amta, Howrah 711401, India
[4]Department of Physical Sciences, IISER Kolkata, Mohanpur 741246, India
[5]Department of Physics, Jadavpur University, Kolkata 700032, India

[a)]Author to whom correspondence should be addressed: shabnam.sabana@gmail.com
[b)]Electronic mail: sudeshna.dasgupta@ladybrabourne.com
[c)]Electronic mail: ghoshaln@yahoo.co.in
[d)]Electronic mail: adg@iiserkol.ac.in
[e)]Electronic mail: roy.soumenkumar@gmail.com

ABSTRACT

Since a rigorous microscopic treatment of a nematic fluid system based on a pairwise interaction potential is immensely complex, we had introduced a simple mean field potential, which was a modification of the Maier–Saupe potential in a previous paper [S. DasGupta *et al.*, "Pressure-induced phase transitions in liquid crystals: A molecular field approach," Phys. Rev. E **98**, 022701 (2018)]. Building upon that, here we have modified that potential to take into account the various aspects of a smectic A–nematic phase transition. In particular, we have studied the dependence of the phase transition on the coupling coefficient between the nematic and smectic order parameters, which in turn depends on the length of alkyl chain, variation of density, entropy, and specific heat. Detailed investigation on the coupling parameter shows the existence of a smectic A–nematic–isotropic triple point as well as a tricritical point where the smectic–nematic phase transition changes its nature from the second to the first order. It is also seen that the application of pressure can result in the appearance of a nematic phase.

I. INTRODUCTION

Maier and Saupe[1] presented a microscopic statistical theory of nematic liquid crystals based on dipole–dipole dispersive interactions. They obtained an orientation-dependent potential between a pair of elongated molecules, which successfully described the first-order nematic–isotropic liquid phase transition in a molecular field approximation. In this theory, only the orientational order parameter was considered. In 1970, Kobayashi[2,3] introduced a theory of melting in liquid crystals for which both the translational and orientational order parameters were taken into account. His formulation was analogous to that of Kirkwood and Monroe.[4] Later in 1971, McMillan[5,6] presented a simple molecular model with anisotropic forces for the smectic A phase by extending the Maier–Saupe molecular potential. Introducing one physical parameter α as a dimensionless interaction strength for the smectic A phase, he predicted that the extent of the nematic range would depend on the value of α. The nematic range decreases as α increases leading to a first-order smectic A–isotropic transition. One gets a triple point (TP) where the three phases, namely, smectic A (A), nematic (N), and isotropic (I) coexist. McMillan calculated the transition temperatures as a function of α and produced a generalized phase diagram to explain the role of alkyl end chains in the formation of the smectic A phase. He was the first to point out that the A–N transition could be second order if $\frac{T_{AN}}{T_{NI}} < 0.87$, where T_{AN} is the A–N and T_{NI} the N–I transition temperatures. Above this value, the A–N transition

is a first-order transition. A change on the order of phase transition is thus expected near $\frac{T_{AN}}{T_{NI}} = 0.87$ giving rise to a tricritical point (TCP). According to this theory, the appearance of a second-order phase transition is related to the saturation of the nematic order at T_{AN}. McMillan's prediction of second-order behavior was subsequently verified experimentally by Doane *et al.*[7] in 1972. With the nuclear magnetic resonance (NMR) study of the homologous series of compounds like 4-n-alkoxybenzylidene-4'-phenylazoaniline, they found that the A–N transition could be second order or very nearly second order. The same qualitative features were presented in the De Gennes[8] model. Using a Landau expansion of smectic A free energy, he showed that the order of the transition depends on α, which is the strength of the coupling between the nematic or orientational order parameter and the smectic A or density order parameter. The alkyl chain length is related to the coupling constant α. As α increases, which in turn increases the coupling between the nematic and smectic A order parameters, the extent of the nematic phase gradually becomes smaller. This favors a first-order A–N phase transition. At lower values of α however, the larger range of the nematic phase saturates the order parameter and the A–N transition becomes second order. A tricritical point exists at the crossover from second- to first-order behavior. The question of the existence of a A–N tricritical point has motivated interest among researchers for several years. Since the theoretical discovery by Kobayashi[2,3] and McMillan,[5,6] there have been several experiments that strongly suggest such a point does exist on phase diagrams of temperature vs pressure[9] or vs concentration of the liquid crystalline material.[10,11] Alben[12] predicted a He^3–He^4 like TCP in binary liquid crystal mixtures. In 1973, Keyes *et al.*[13] reported a pressure study for the transition between the smectic A and cholesteric liquid crystalline phases of cholesteryl oleyl carbonate and discovered a new type of TCP. However, Halperin, Lubensky, and Ma[14,15] argued that the A–N transition can never be truly second order, thus, ruling out conventional tricritical behavior. The trend of three phases meeting at a single point was experimentally found by Shashidhar and Chandrasekhar[16] when they investigated the pressure dependence for methoxybenzoic acid and ethoxybenzoic acid. This work not only supported the appearance of a triple point (TP) in liquid crystalline systems but also established for the first time the existence of the solid-nematic–isotropic and solid-smectic A–nematic triple points in a single component system. This investigation gave a detailed insight on the effect of pressure on the liquid crystalline phase transitions confirming the presence of a tricritical point (TCP) at 2.66 kbar as predicted by Keyes *et al.*[13] Later in 1979, Brisbin *et al.*[17] reported the presence of tricritical point in the homologous series pentylbenzenethioalkoxybenzoate by their specific heat and birefringence measurements. Thoen *et al.*[18] in 1984 also showed by using adiabatic-scanning calorimetry that although A–N transition is first order for very narrow N ranges, it is second order for large N ranges in the series alkoxycyanobiphenyl. Up until many experiments and theories[19–27] have confirmed this trend of appearances of TP and TCP for many liquid crystal materials and liquid crystal mixtures.

In 2018 (Ref. 28), we had presented a molecular field theory to study pressure induced phase transitions in liquid crystals. A simple effective potential was chosen to discuss, in particular, the N–I phase transition. In the present paper, we intend to demonstrate the utility of our model in a more general case. Following McMillan's molecular model, we have extended the potential for studying the A → N → I phase transitions. The purpose of this paper is to study the pressure dependence and thermodynamics of liquid crystalline phase transitions. We have compared both qualitatively and quantitatively the results obtained by our methods with the existing theoretical and experimental results. We have found that given the simplicity of the model the agreement is quite good.

II. OUR MODEL

One of the pioneering works in theoretical modeling of liquid crystals was by Maier and Saupe[1] who in order to explain the orientational order in nematics introduced the potential

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

Here, A is a constant and v is the volume of the fluid per molecule. $P_2(x)$ is the second-order Legendre polynomial, which is given by the mathematical expression $\frac{1}{2}(3x^2-1)$. ϑ is the angle between the director and the molecular long axis. $\langle P_2\rangle$ denotes the orientational order parameter.

For any smectic A liquid crystal, there is an additional one-dimensional translational periodicity, which requires some degree of translational order in addition to the long-range orientational order for characterizing the phase. McMillan[5] developed Eq. (1) further to account for the possibility of a smectic A phase. Any realistic theoretical model of liquid crystals which allow volume fluctuation must include both repulsive and attractive interactions. In Ref. 28, we had used a molecular field approach by adapting the Maier–Saupe potential for this purpose by adding an isotropic volume dependent term. In this paper, we further extend that work by following the development by McMillan[5] that included another term to account for the translational periodicity. We have used this to study the liquid crystalline smectic A to nematic phase transition. The effective single particle potential we choose for this purpose is given by

$$U = \frac{u_4}{v^4} - \frac{u_2}{v^2} - \frac{Au_2}{v^2}\left[\langle P_2\rangle P_2(\cos\vartheta) + \alpha\left\langle P_2(\cos\vartheta)\cos\left(\frac{2\pi z}{d}\right)\right\rangle P_2(\cos\theta)\cos\left(\frac{2\pi z}{d}\right)\right], \tag{2}$$

where u_4, u_2, and α are constants and v is the volume of the fluid per molecule. A is a phenomenological constant that expresses the relative strength of the anisotropic interaction in comparison to the attractive part of the isotropic term. Here, the volume dependence of the isotropic terms has been chosen to mimic the scaling behavior of the familiar Lennard–Jones potential. The repulsive term $\frac{u_4}{v^4}$ ensures that the molecules do not collapse to zero volume under the attraction, while the attractive term $\left(-\frac{u_2}{v^2}\right)$ serves to ensure that the molecules do not move too far apart. d is the spacing between two smectic layers along the z direction. This spacing is approximately of a molecular length. We have considered the isothermal–isobaric ensemble that consists of systems which can exchange energy with each other and undergo volume fluctuations while maintaining constant temperature (T), pressure (P), and number of particles (N). This kind of ensemble is denoted as the NPT ensemble. Alternatively we can think of this as a single system with non-rigid diathermal walls in contact with a temperature and pressure reservoir.

Using this potential, the canonical partition function can be written as

$$Z_{NVT} = \frac{V^N}{N!\Lambda^{3N}}\left(\bar{Z}_1 \exp\left(\frac{\beta}{2}\langle U\rangle\right)\right)^N \times \exp\left[-N\beta\left(\frac{u_4}{\nu^4}-\frac{u_2}{\nu^2}\right)\right], \quad (3)$$

where

$$\bar{Z}_1 = \frac{1}{d}\int_0^d \int_0^1 I(\cos\vartheta, z)\, d(\cos\vartheta)\, dz \quad (4)$$

is the single particle partition function and

$$I(\cos\vartheta, z) = \exp\left[\frac{\beta A u_2}{\nu^2}\left(\langle P_2\rangle P_2(\cos\vartheta) + \alpha\left\langle P_2(\cos\vartheta)\cos\left(\frac{2\pi z}{d}\right)\right\rangle\left(P_2(\cos\vartheta)\cos\left(\frac{2\pi z}{d}\right)\right)\right)\right]$$

is the distribution function.

Here, $\beta = 1/KT$, d is the layer thickness, N is the total number of particles in the system, and V is the volume of the system.

Hence, the partition function for the NPT 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

$$f(v) = -\beta p v + \ln v + \ln \bar{Z}_1 - \frac{A u_2 \beta}{2\nu^2}(\eta^2 + \alpha\sigma^2) - \frac{\beta}{2}\left(\frac{u_4}{\nu^4}-\frac{u_2}{\nu^2}\right), \quad (7)$$

where V_0 is the normalization constant, $\Lambda = \left(\frac{C}{\beta}\right)^{\frac{1}{2}}$ with C a constant. $\eta = \langle P_2(\cos\vartheta)\rangle$ denotes the purely orientational (i.e., nematic) order parameter and $\sigma = \langle P_2(\cos\vartheta)\cos\left(\frac{2\pi z}{d}\right)\rangle$ denotes the mixed order parameter, which describes the coupling between the degrees of orientational and translational order. As in McMillan,[5] we neglect the purely translational order parameter for the simplicity reason.

$f(v)$ depends on v, $\langle P_2(\cos\vartheta)\rangle$, $\langle P_2(\cos\vartheta)\cos\left(\frac{2\pi z}{d}\right)\rangle$ and on the constant parameters p, β, u_2, u_4, α, 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 (the details of the calculation can be found in Ref. 28) to write (upto a multiplicative constant which we ignore)

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

where ν_* is the value of ν, which maximizes $f(\nu)$.

Maximizing $f(\nu)$, we get the equation of state

$$p - \frac{1}{\beta\nu_*} - \frac{2u_4}{\nu_*^5} + \frac{u_2}{\nu_*^3}\left[1 + A\eta^2 + A\alpha\sigma^2\right] = 0. \quad (9)$$

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

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

up to a constant. Hence, the Gibb's free energy of the system in units of KT is given by

$$G\beta = N\left(p\beta\nu_* - \ln\nu_* + \frac{\beta}{2}\frac{u_4}{\nu_*^4} - \frac{\beta u_2}{2\nu_*^2} - \ln\bar{Z}_1(\lambda,\mu) + \frac{\beta}{2}\left(\frac{A u_2 \eta^2}{\nu_*^2} + \frac{A u_2 \alpha\sigma^2}{\nu_*^2}\right)\right) - \frac{3N}{2}\ln\beta, \quad (10)$$

where $\lambda = \frac{A u_2 \beta}{\nu^2}\eta$ and $\mu = \frac{A u_2 \beta\alpha}{\nu^2}\sigma$.

Now by minimizing Eq. (10) w.r.t λ and μ, we obtain

$$\eta = \frac{1}{\bar{Z}_1}\left(\frac{\partial \bar{Z}_1(\lambda,\mu)}{\partial\lambda}\right) \quad (11)$$

and

$$\sigma = \frac{1}{\bar{Z}_1}\left(\frac{\partial \bar{Z}_1}{\partial\mu}\right). \quad (12)$$

Solving Eqs. (9), (11), and (12) simultaneously, we obtain the value of η, σ, and ν_* for the different liquid crystalline phases. Again solving Eq. (9) for $\eta = \sigma = 0$ yields the value of ν_* for the isotropic phase. Similarly, the condition $\eta = 0$ and $\sigma \neq 0$ yields the smectic A phase and $\sigma = 0$ and $\eta \neq 0$ yields the nematic phase. Out of these possibilities, the equilibrium value of η, σ, and ν_* for a particular set of constant parameters p, β, u_2, u_4, α, and A is decided by checking which of these yield the lower value of G. This value of ν_*, η, and σ globally minimizes the function G.

Now we obtain the critical constants p_c, β_c, and ν_c for the isotropic-vapor transition from Eq. (9) (setting $\eta = \sigma = 0$) in terms of u_2 and u_4,

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

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

$$p_c\beta_c\nu_c = \frac{8}{15}. \quad (15)$$

To get rid of the constants u_2 and u_4, we have expressed the temperature (T), pressure (p), and volume (ν) in terms of reduced parameters $\vartheta = \frac{T}{T_c}$, $\pi = \frac{p}{p_c}$, $\omega = \frac{\nu}{\nu_c}$.

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

$$\pi = \frac{15\vartheta}{8\omega} + \frac{3}{8\omega^5} - \frac{5}{4\omega^3}\left(1 + A\eta^2 + A\alpha\sigma^2\right). \quad (16)$$

The corresponding free energy in terms of the reduced set of parameters π, ω, and ϑ is

$$G_R = \frac{8\pi\omega}{15\vartheta} - \ln\omega + \frac{1}{20\vartheta\omega^4} + \frac{1}{3\vartheta\omega^2}\left(A\eta^2 + A\alpha\sigma^2 - 1\right) - \ln\bar{Z}_1(\lambda,\mu) + \frac{3}{2}\ln\vartheta. \quad (17)$$

Using Eqs. (16) and (17), we obtained the values of η, σ, and ω. Again solving Eq. (16) for $\eta = \sigma = 0$ yields the value of ω for the isotropic phase. As discussed earlier out of these two values the equilibrium value of η, σ, and ω is decided on the basis of which of these values yields a lower G_R.

The entropy in the reduced form is

$$S = \frac{S'}{Nk} = -\frac{2A}{3\vartheta\nu^2}\left(\eta^2 + \alpha\sigma^2\right) + \ln\left(\bar{Z}_1(\lambda,\mu)\right). \quad (18)$$

We have calculated the specific heat at constant pressure using the equation

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p, \tag{19}$$

where the derivative has been evaluated numerically.

III. RESULTS AND DISCUSSION

In this section, the results obtained using our model potential have been discussed and compared with the existing theoretical and experimental results. In our model, A and α are free parameters, which can be varied to match different liquid crystalline systems. For example, the value of $A = 0.675$ and $\alpha = 0.494$ helped us fit the experimental data of A–N transition temperature ($T_{AN} = 343$ K) and the N–I transition temperature ($T_{NI} = 353$ K) for 8OCB quite well.

A. Effect of pressure on the order parameters

The variation of order parameters η and σ with temperature at two different values of pressure is shown in Fig. 1. The model parameter α is taken to be 0.55. The left diagram shows variation at $P = 1$ bar and the right one at $P = 14.3$ bar. The effect of pressure on the A–I or A–N transition is to increase the transition temperature as can be seen from the figure. This is because of the fact that an increase in pressure brings about more order in the liquid crystal molecules. From the variation of the σ curve, the A–I or A–N transition is found to be of first order even at elevated pressure. It is also seen that as pressure increases, the discontinuity of the σ curve, at the transition, decreases. This result is in accordance with the work by Mukherjee and Rzoska[26] in 2002. Another interesting feature is the appearance of the pressure-induced nematic phase at higher pressure as can be seen following the η curve.

B. Effect of temperature on the order parameters

The pressure dependence of the order parameters η and σ is shown in Fig. 2 for three representative values of temperature. At $T = 360$ K, there is a direct smectic A to isotropic transition while at the higher T values, that is, at $T = 380$ K and $T = 400$ K nematic phase is also present. Here, as expected, we can see the A–N transition at P_{AN} and subsequently a N–I transition at P_{NI} for the lower values of

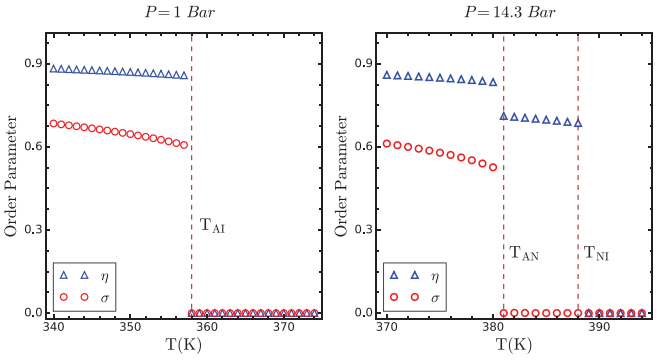


FIG. 1. Variation of order parameters η and σ with temperature at different values of pressure.

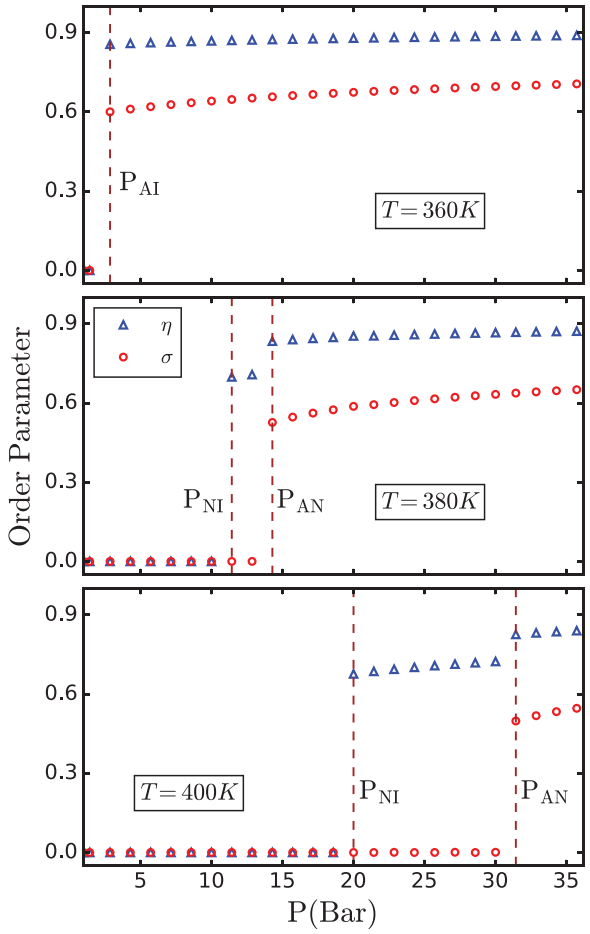


FIG. 2. Variation of order parameters η and σ with pressure at various fixed values of temperature.

pressure. It can be noted that the value of order parameters decreases with the decrease in pressure in each case, thereby showing that the liquid crystalline system becomes less and less ordered as pressure decreases.

C. Effect of pressure and temperature on the density

Another important quantity that we can look at is the variation of density (ρ) with pressure and temperature. Figure 3 shows the pressure (left figure) and temperature (right figure) dependence of the density (ρ) of the system. As P increases, ρ increases leading to $I \rightarrow N \rightarrow A$ transitions. However, larger values of T cause decrease in ρ leading to $A \rightarrow N \rightarrow I$ transitions. These results are consistent with the usual behavior of any liquid crystalline material, and as expected, we find discontinuities in ρ at the phase transitions.

D. Significance of the model parameter α

The physical parameter α acts as a dimensionless interaction strength for the smectic A phase. From the theoretical point of view, α is related to the length of the alkyl chain in a homologous series such

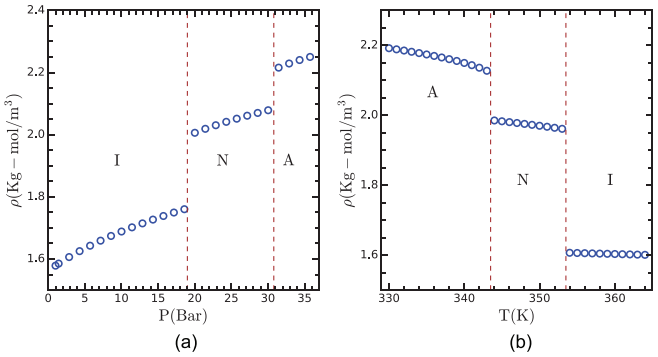


FIG. 3. Variation of density (ρ) with (a) pressure at fixed temperature $T = 400$ K and (b) temperature at fixed pressure $P = 1$ bar.

that α should increase with increasing chain length. Following the McMillan theory,[5] we have taken different values of the constant α to discuss the variation of liquid-crystal behavior in a homologous series. In the following discussions, we have showed how the temperature and pressure phase diagrams vary with the model parameter α.

1. α phase diagram

The transition temperatures ($\frac{T}{T_{NI}}$) as a function of the model parameter α are plotted in Fig. 4(a), where $T_{NI} = 353$ K, the N–I transition temperature for all $\alpha < 0.53$. The phase diagram shows that at lower values of α all three phases, namely, smectic A, nematic, and isotropic exist and, A $\rightarrow$ N $\rightarrow$ I phase transitions occur as temperature is increased. For higher values of α ($\alpha > 0.53$), only smectic A and isotropic phases can be observed and a direct A–I transition takes place. $\frac{T}{T_{NI}} = 1$ represents the N–I transition line upto $\alpha = 0.53$. The A–N transition temperature is an increasing function of α and reaches the N–I line at $\alpha = 0.53$. All these three phase transition lines, A–N, N–I, and A–I, as can be seen from Fig. 4(a), meet at ($\alpha = 0.53$, $\frac{T}{T_{NI}} = 1$), and thus, form a triple point (TP). The T_{AN} curve is very nearly a continuation of the T_{AI} curve at the triple point as expected from the theoretical model.

Another interesting feature can be pointed out from Fig. 4(a). The A–N transition line is second order for all $\alpha < 0.4$ (this has been indicated by the filled blue circles in the phase diagram) and is first order for $0.4 < \alpha < 0.53$ (this has been indicated by the open blue circles in the phase diagram). This confirms the presence of a tricritical point (TCP) at $\alpha = 0.39$ and $\frac{T_{AN}}{T_{NI}} = 0.866$. This phase diagram is seen to give an excellent qualitative agreement with McMillan's model.[5]

The transition pressures ($\frac{P}{P_{NI}}$) as a function of the model parameter α are plotted in Fig. 4(b) where $P_{NI} = 18.6$ bar, the N–I transition pressure for all $\alpha < 0.60$. At lower values of α, all three phases exist and I $\rightarrow$ N $\rightarrow$ A phase transitions occur as pressure is increased. For higher values of α ($\alpha > 0.60$), only smectic A and isotropic phases can be observed and a direct I–A transition takes place. $\frac{P}{P_{NI}} = 1$ represents the N–I transition line upto $\alpha = 0.60$. The A–N transition pressure is a decreasing function of α and reaches the N–I line at $\alpha = 0.60$. All these three phase transition lines, A–N, N–I, and A–I, as can be seen from Fig. 4(b), meet at ($\alpha = 0.60$, $\frac{P}{P_{NI}} = 1$), and thus, form a triple point (TP). The P_{AN} curve is very nearly a continuation of the P_{AI} curve at the triple point.

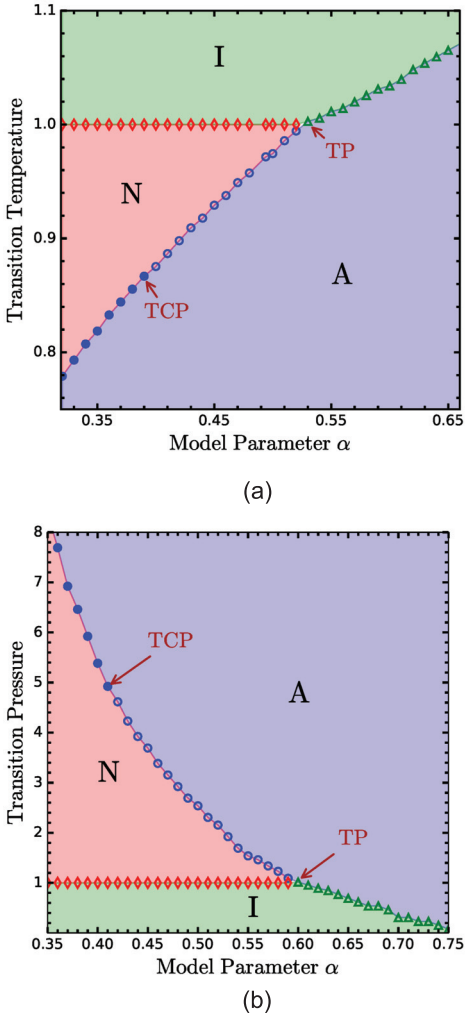


FIG. 4. Phase diagram with the variation of the model parameter α (a) with temperature at $P = 1$ bar (atmospheric pressure) and (b) with pressure at $T = 400$ K. The lines separate the regions of stability of the smectic A (A), nematic (N), and isotropic (I) phases. Red line (diamond points) corresponds to the N–I transition, the blue line (circular points) is the A–N transition and the green line (triangular points) is the A–I transition. Filled and open blue circles on the A–N transition line indicate second-order and first-order phase transitions, respectively.

From Fig. 4(b), it is seen that the A–N transition line is second order for all $\alpha < 0.42$ (this has been indicated by the filled blue circles in the phase diagram) and is first order for $0.42 < \alpha < 0.60$ (this has been indicated by the open blue circles in the phase diagram). Thus, the pressure study of α also confirms the presence of a TCP at $\alpha = 0.41$ and $\frac{P_{AN}}{P_{NI}} = 4.9$.

2. Thermodynamic variables at different values of α

To illustrate the above behavior of α phase diagram (Fig. 4), in this section we shall discuss the order parameters η and σ, the entropy

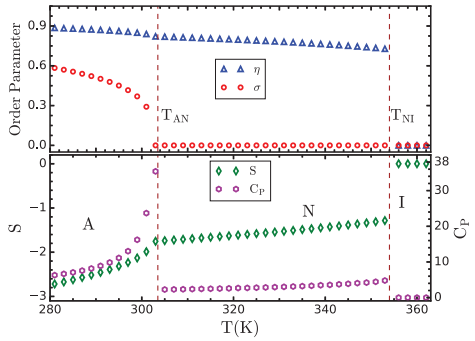
S and the specific heat C_P as a function of temperature for three different values of interaction strength α.

For $\alpha = 0.38$ [Fig. 5(a)], the A–N transition is second order as the smectic order parameter σ falls continuously to 0 at the transition ($\frac{T_{AN}}{T_{NI}} = 0.85$). The corresponding N–I transition is, however, first order in nature as denoted by a discontinuous jump at T_{NI}. Entropy (S) and specific heat (C_P) also show similar kind of behavior. We can see that the entropy changes continuously at the A–N transition indicating a second order but has a discontinuous jump at the N–I transition favoring first-order phase transition. In the case of C_P, we get discontinuous jump at both the transitions but quantitatively the value of discontinuity at the N–I transition is larger than that at the A–N transition.

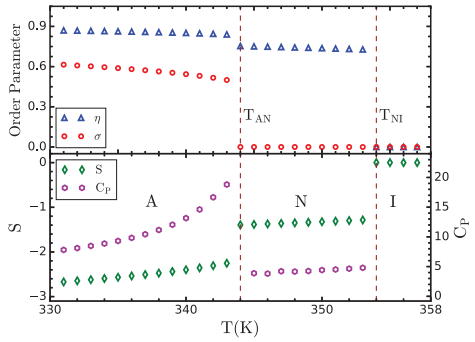
For $\alpha = 0.494$ [Fig. 5(b)], the A–N transition is first order as σ drops discontinuously to 0 at the transition ($\frac{T_{AN}}{T_{NI}} = 0.97$). The corresponding N–I transition is also first order in nature. The discontinuity in S and C_P at both transitions show that they are first-order transitions.

For $\alpha = 0.55$ [Fig. 5(c)], a direct A–I transition occurs. Both order parameters σ and η drop discontinuously to 0 at T_{AI}. The discontinuity in S and C_P shows that the A–I transition is a first-order transition.

All these calculations have been performed at the atmospheric pressure $P = 1$ bar.



(a)



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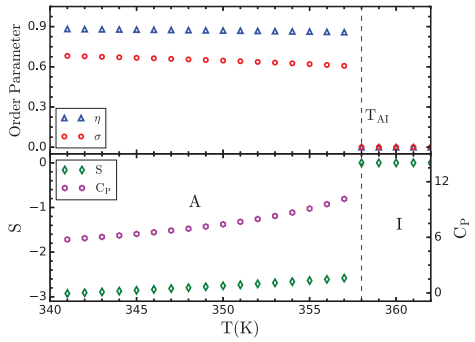

(c)

FIG. 5. Variation of order parameters σ, η, entropy S, and specific heat C_P with temperature are shown for three different values of α at the atmospheric pressure. (a) At $\alpha = 0.38$, the smectic A–nematic transition is second order and the nematic–isotropic liquid transition is first order. (b) At $\alpha = 0.494$, both smectic A–nematic and nematic–isotropic liquid transitions are first order. (c) At $\alpha = 0.55$, only smectic-A–isotropic liquid transition is present and this is first order in nature.

3. Phase diagrams at different values of α

A detailed investigation on the pressure and temperature dependence of a liquid crystalline system at different values of α has been carried out. Here, we have discussed the phase diagrams for three different values of α.

For $\alpha = 0.494$ [Fig. 6(a)], we have the phase diagram denoting the smectic A, nematic, and isotropic liquid phases. As the pressure is raised, both the A–N and N–I transition temperatures increase. It is also seen from the diagram that the slope $\frac{dT}{dP}$ for the N–I transition line is greater than that of A–N transition line. This kind of behavior is also expected according to the Clausius–Clapeyron equation. For our choice of parameters, this phase diagram [Fig. 6(a)] reproduces the known behavior of cyano-octyloxybiphenyl (8*OCB*) as shown by Cladis *et al.*[27] in their experimental work.

The phase diagram for the model parameter $\alpha = 0.55$ is shown in [Fig. 6(b)]. At lower pressure, there is only one transition, namely, smectic A to isotropic (A–I) transition. At higher pressure, the nematic phase appears and there are two transitions, namely, A–N and N–I transitions. The branching point from where A–N and N–I transition lines originate from the A–I transition line is called the triple point (TP). With our specific choice of parameter values, we get TP at 368.12 K, 6.14 bar. Experimentally, the appearance of such smectic A–nematic–isotropic TP was found by Lampe and Collings[20] in the ninth member such as in the homologous series of dialkylazoxybenzenes (9*AB*).

With higher value of α, the nature of phase diagram changes completely. Figure 6(c) shows the phase diagram for $\alpha = 0.85$. Here, we can see that our system undergoes a direct transition from the smectic A to the isotropic phase without going through the nematic phase. Qualitatively, this can be attributed to the high value of α, which in turn signifies liquid crystalline molecules with long alkyl chains. This can be seen in the homologous series of cyanobiphenyls (e.g., 10*CB* or 12*CB* as shown in Ref. 29).

IV. CONCLUSIONS

We have presented a simple model potential with parameter A and α. The properties of thermotropic liquid crystalline systems such as the order parameters, density, entropy, and specific heat are investigated with the variation of temperature and pressure. All of these quantities reproduce much of the known behavior of a smectic A–nematic–isotropic liquid phase transitions. Our study shows that

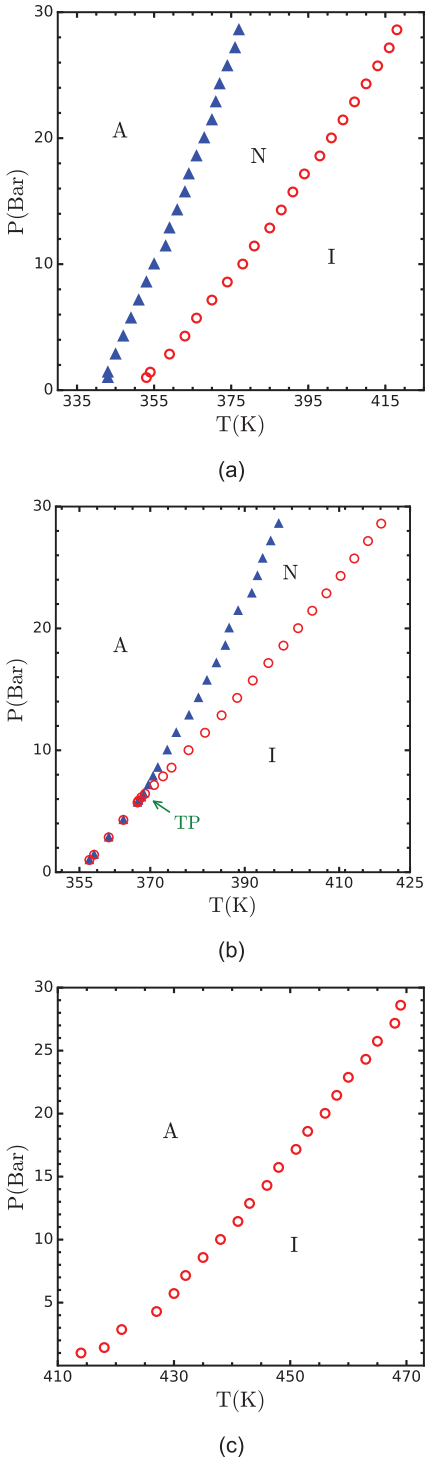

FIG. 6. *P–T* phase diagram at different values of α. (a) At $\alpha = 0.494$, all the three phases: smectic A, nematic and isotropic liquid are present. (b) At $\alpha = 0.55$, the smectic A–nematic and nematic–isotropic phase boundaries intersect at 368.12 K and 6.14 bar and form a smectic A–nematic–isotropic triple point (TP). (c) At $\alpha = 0.85$, no nematic phase only smectic A and isotropic liquid phases are present.

smectic A–nematic and nematic–isotropic liquid transition temperatures depend on pressure as well as on the parameter value α. It has been seen that the application of pressure strongly affects the stability of the nematic phase. As a result of which the nematic phase can disappear and a direct transition from the smectic to isotropic phase occurs. On the other hand, as α value changes the nature of *P–T* phase diagram changes drastically. For lower value of α, two phase boundaries: smectic A–nematic and nematic–isotropic are present. However, at slightly higher value of α, smectic A–nematic and nematic–isotropic phase boundaries meet at the smectic–isotropic phase boundary. This meeting point is the smectic A–nematic–isotropic triple point. At much higher value of α, only smectic–isotropic phase boundary is present. Thus, the nematic phase disappears at higher value of α. In the present paper, we have chosen $A = 0.675$ and $\alpha = 0.494$, which helped us fit experimental data for 8*OCB* quite well. Based on these findings, we believe that different values of the parameters A and α can be chosen to study different liquid crystalline materials.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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