Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Pressure-driven reentrant phenomena in liquid crystals: the role of inverse layer spacing

Shri Singh[a]; Amit Srivastava[a]; Debanand Sa[a]
[a] Department of Physics, Banaras Hindu University, Varanasi, India

Online publication date: 11 February 2010

To cite this Article Singh, Shri , Srivastava, Amit and Sa, Debanand(2010) 'Pressure-driven reentrant phenomena in liquid crystals: the role of inverse layer spacing', Liquid Crystals, 37: 2, 227 — 232
To link to this Article: DOI: 10.1080/02678290903502015
URL: http://dx.doi.org/10.1080/02678290903502015

Liquid Crystals,
Vol. 37, No. 2, February 2010, 227–232

Taylor & Francis
Taylor & Francis Group

Pressure-driven reentrant phenomena in liquid crystals: the role of inverse layer spacing

Shri Singh*, Amit Srivastava and Debanand Sa

Department of Physics, Banaras Hindu University, Varanasi -221005, India

(Received 7 July 2009; final version received 20 November 2009)

The occurrence of pressure-driven reentrant phenomena observed in high-pressure experimental studies in some achiral mesogenic materials has been explained using a thermodynamic model based on Landau–de Gennes theory. In this approach, the free-energy is expanded in terms of nematic, smectic A order parameters and the couplings (cubic and biquadratic) between them. The basic theme here is that the 'inverse layer spacing', which mimics an order parameter, becomes coupled to the nematic and smectic A order parameters. Secondly, in addition to the order parameter couplings the N–S_A metastable temperature (which appears due to elimination of inverse layer spacing from the free-energy density expression) becomes pressure dependent. The occurrence of a pressure-driven reentrant nematic phase is explained in terms of these three pressure-dependent parameters. They all show smooth but rapid variation at the critical pressure beyond which nematic reentrance appears.

Keywords: liquid crystals; reentrant phenomena; phase transitions; Landau–de Gennes theory

1. Introduction

The phenomenon of reentrant phase transition, that is an occurrence of a low symmetric phase in between two high symmetric phases, is intrinsically novel and the sustained interest in this problem is underlined by its discovery in amazingly diverse classes of condensed matter systems [1–17]. In achiral liquid crystals, the nematic (N)–partial bilayer smectic A (S_{A_d})–reentrant nematic (N_R)–monolayer smectic A (S_{A_1}) phase sequence was first reported by Cladis [18] in a mixture of {p-[p-hexyloxybenzylidene-amino] benzonitrile} (HBAB) and [N-p-cyanobenzylidene-p-n-octyloxyaniline] (CBOOA). It has also been observed [19–21] that the reentrance can be driven by increasing pressure in pure compounds and their mixtures. X-ray and microscopy studies showed [22,23] that the reentrant nematic phase is similar to the classical nematic phase but may coexist with crystalline fluctuations. Both the nematic phases are uniaxial and the defect structure of the N_R phase observed in cylindrical geometry is identical to that of the N phase. The phase sequence of multiple reentrance has been observed in several mesogenic compounds.

The phenomenon of reentrant polymorphism in liquid crystals is very rich [3,6]. However, the origin of the occurrence of reentrance is still an unsolved problem in condensed state and statistical mechanics. From mere energy–entropy arguments the appearance of the reentrant phase is inexplicable. Its microscopic origin varies from system to system and is still debatable in many cases. In the case of liquid crystals, only qualitative explanations have been possible. The first tentative explanation was given by Cladis [19] herself in which it was assumed that the forces stabilising the layers (the S_A phase) are the short-range attractive hydrocarbon (non-polar–non-polar) interactions and that the increasing repulsive interaction of the aromatic rings with increasing pressure drives the layers apart giving rise to the N_R phase. A number of other elaborate models (for details see [1,3,6]) have been proposed for explaining the occurrence of reentrant phases. de Miguel and del Rio [24] have performed a computer simulation study under pressure for the nematic reentrance in a system of parallel hard ellipsoids with the attractive interaction represented by a spherically symmetric square well.

There exists another line of thought to account for the reentrance phenomena in liquid crystals, that is, the Landau–de Gennes phenomenological approach. In this approach, the free-energy density is written as an expansion series in terms of order parameters and their couplings. Cladis [25] proposed a free-energy expression to explain the occurrence of the N_R phase by considering the temperature dependence in the biquadratic coupling between the nematic and smectic order parameters. Vaz and Doane [26] showed that the expansion of the free-energy excess in terms of order parameters containing a temperature-independent coupling term can give rise to the reentrant transition. Lelidis and Durand [27] proposed a free-energy density to describe, under electic field, the paranematic–non-spontaneous nematic (pN–NSN), non-spontaneous nematic–smectic A (NSN–S_A), nematic–smectic A (N–S_A), isotropic–smectic A (I–S_A) and smectic

*Corresponding author. Email: srisingh@rediffmail.com

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290903502015
http://www.informaworld.com

A–reentrant nematic (S_A–N_R) phase transitions in achiral mesogens. These phase sequences were described by varying the coupling between the orientational and positional order parameters. In the free energy a cubic and a biquadratic coupling terms were included. It is argued that the presence of a large and positive coefficients for the biquadratic coupling yields a reentrant nematic phase.

In two previous papers [28,29] of this series within the framework of the Landau–de Gennes formulation we investigated the influence of pressure on the phase transition properties of achiral liquid crystals. The effect of pressure on the electric-field-induced phase transitions in a system showing a spontaneous isotropic–smectic A transition was analysed in the first paper [28] by incorporating the pressure influence in the mean-field model through $|\nabla\psi|^2$ as well as the coupling between the tensor nematic order parameter Q_{ij} and $|\nabla\psi|^2$ terms. In the second paper [29], we extended the Landau–de Gennes formulation [27] to study the pressure variation of the reentrant transition in a mesogenic material exhibiting the isotropic–nematic–smectic A phase sequence on cooling. Using the same phenomenological approach, in the present work we have analysed the role of inverse layer spacing on the origin of the occurrence of the pressure-driven reentrance phenomenon. We study the pressure variation of the reentrant transition in liquid crystals in mesogens exhibiting the I–N–S_A transition on cooling. Based on the high-pressure experimental studies of the temperature–pressure (*T–P*) phase diagram as well as the 'inverse layer spacing' data, we explain the occurrence of the reentrant nematic phase within the framework of the Landau–de Gennes phenomenological formalism in which the effect of wave vector q_0 fluctuations has been accounted for. In this formulation not only do the couplings between the nematic and smectic order parameters become pressure dependent but also the metastable temperature (which appears due to the elimination of q_0 from the free energy). Unlike the earlier phenomenological approach, here pressure-dependent Landau coefficients are needed to describe the pressure-driven reentrant phenomena. Furthermore, the pressure variation of all these parameters is computed over a wide range of pressure. This paper is organised as follows. The effective free energy, and the renormalised N–S_A transition temperature are derived in Section 2. In Section 3 the occurrence of the reentrant phenomenon is discussed and the importance of the present formulation as compared to the earlier phenomenology is outlined. The final Section 4 is devoted to the main findings of the present work and its future prospects are summarised.

2. Theoretical framework and working equations

We consider a mesogenic system which exhibits an isotropic–nematic–smectic A (I–N–S_A) phase sequence on cooling. The nematic and smectic phases reflect symmetry breaking related to different degrees of freedom. Nematic ordering deals with the local probability distribution of molecular orientation $f(\hat{\mathbf{e}})$, where $\hat{\mathbf{e}}$ is the unit vector along the molecular axis, and it is described by a traceless tensor order parameter $\mathbf{Q}_{ij} = \frac{S}{2}(3\hat{\mathbf{n}}_i\hat{\mathbf{n}}_j - \delta_{ij})$ with $\hat{\mathbf{n}}$ as the director and $0 \leq S \leq 1$ the order modulus. The smectic ordering refers to the distribution in space of the molecular mass centres. In a smectic phase, the molecules tend to organise themselves in a layered structure. The complex smectic order parameter $\psi(r) = \psi_0 \exp(-i\phi)$ measures the inhomogeneity of the spatial molecular density. ψ_0 is defined as the amplitude of the one-dimensional density wave characterised by a phase ϕ. In the S_A phase the wave vector $\nabla_i\phi$ is parallel to the director $\hat{\mathbf{n}}$, $q_0 = |\nabla\phi|$ and $d = 2\pi/q_0$ gives the layer spacing. The free-energy density f_T of the system can be written as

$$f_T = f_0 + f_{\mathrm{N}}(T, Q) + f_{\mathrm{A}}(T, \psi) + f_{\mathrm{NA}}(T, Q, \psi), \quad (1)$$

where f_0, f_N and f_{A} are, respectively, the free-energy density of the isotropic, nematic and smectic A phases and f_{NA} is that of the coupling between the N and S_A order parameters. f_{N}, f_{A} and f_{NA} can be expanded in terms of the order parameters and the couplings between them as [30]

$$f_{\mathrm{N}} = \frac{1}{2}A_{\mathrm{N}}Q_{ij}Q_{ij} + \frac{1}{3}b_{\mathrm{N}}Q_{ij}Q_{jk}Q_{ki} + \frac{1}{4}c_1(Q_{ij}Q_{ij})^2 + \frac{1}{4}c_2Q_{ij}Q_{jk}Q_{kl}Q_{li}, \quad (2)$$

$$f_{\mathrm{A}} = \frac{1}{2}A_{\mathrm{A}}|\psi|^2 + \frac{1}{4}c_{\mathrm{A}}|\psi|^4 + \frac{1}{2}b_1|\nabla_i\psi|^2 + \frac{1}{2}b_2|\Delta\psi|^2, \quad (3)$$

and

$$f_{\mathrm{AN}} = \frac{1}{2}\lambda|\psi|^2Q_{ij}Q_{ij} + \frac{1}{2}e_1Q_{ij}(\nabla_i\psi)(\nabla_j\psi^*). \quad (4)$$

Here only the coefficients A_{N} and A_{A} of the terms quadratic in the order parameters are assumed to be temperature dependent,

$$A_{\mathrm{N}} = a_{\mathrm{N}}(T - T^*_{\mathrm{NI}})$$

and

$$A_{\mathrm{A}} = a_{\mathrm{A}}(T - T^*_{\mathrm{AN}}). \quad (5)$$

T^*_{NI} represents the lowest temperature at which the isotropic phase is metastable and T^*_{AN} is the lowest temperature of the uncoupled system at which the nematic phase is unstable.

The motivation behind starting with the above free-energy is obvious. This can generate terms in the free energy where the inverse layer spacing parameter q_0 becomes coupled to the nematic and smectic order parameters. This can be obtained following the work of Mukherjee *et al.* [30] where both the nematic and smectic order parameters are considered to be spatially invariant. Thus Equation (1) may be written as

$$f_T = f_0 + \frac{3}{4}A_{\mathrm{N}}S^2 + \frac{1}{4}b_{\mathrm{N}}S^3 + \frac{9}{16}c_{\mathrm{N}}S^4 + \frac{1}{2}A_{\mathrm{A}}\psi_0^2 + \frac{1}{4}c_{\mathrm{A}}\psi_0^4 + \frac{1}{2}b_1\psi_0^2q_0^2 + \frac{1}{2}b_2\psi_0^2q_0^4 + \frac{3}{4}\lambda S^2\psi_0^2 + \frac{1}{2}e_1S\psi_0^2q_0^2. \tag{6}$$

It is apparent from this free-energy that the parameter q_0 mimics an order parameter and it becomes coupled not only to ψ_0^2 but also to $S\psi_0^2$. However, we would like to derive an effective free energy in terms of the order parameters S and ψ_0 only such that it provides the basic theoretical framework for reentrant phenomena. This is, in general, done by minimising Equation (6) with respect to q_0 and ψ_0, which gives the following relations:

$$q_0^2 = -\frac{1}{2b_2}(b_1 + e_1S), \tag{7}$$

$$\psi_0^2 = \frac{-1}{c_{\mathrm{A}}}\left[\left(A_{\mathrm{A}} - \frac{b_1^2}{4b_2}\right) - \frac{e_1b_1}{2b_2}S + \frac{3}{2}\left(\lambda - \frac{e_1^2}{6b_2}\right)S^2\right], \tag{8}$$

where S satisfies a cubic equation

$$-\frac{4\gamma A^*_{\mathrm{A}}}{3c_{\mathrm{A}}} + 2AS + bS^2 + 3cS^3 = 0. \tag{9}$$

Here $A = A_{\mathrm{N}} - \lambda_{\mathrm{eff}}A^*_{\mathrm{A}}/c_{\mathrm{A}} - 4\gamma^2/3c_{\mathrm{A}}$, $b = b_{\mathrm{N}} - 6\gamma\lambda_{\mathrm{eff}}/c_{\mathrm{A}}$, $c = c_{\mathrm{N}} - \lambda^2_{\mathrm{eff}}/c_{\mathrm{A}}$, $A^*_{\mathrm{A}} = A_{\mathrm{A}} - b_1^2/4b_2$, $\gamma = -e_1b_1/4b_2$ and $\lambda_{\mathrm{eff}} = \lambda - e_1^2/6b_2$.

The above minimisation scheme allows us to recast Equation (6) as an effective free energy near the N–S$_{\mathrm{A}}$ transition in terms of the renormalised parameters which looks exactly similar to the free energy considered by Lelidis and Durand [27], that is,

$$f = f_0 + \frac{3}{4}A_{\mathrm{N}}S^2 + \frac{1}{4}b_{\mathrm{N}}S^3 + \frac{9}{16}c_{\mathrm{N}}S^4 + \frac{1}{2}A^*_{\mathrm{A}}\psi_0^2 + \frac{1}{4}c_{\mathrm{A}}\psi_0^4 + \gamma S\psi_0^2 + \frac{3}{4}\lambda_{\mathrm{eff}}\psi_0^2S^2. \tag{10}$$

Here T^*_{AN} is renormalised to $\bar{T}_{\mathrm{AN}} = T^*_{\mathrm{AN}} + T'_{\mathrm{AN}}$; $T'_{\mathrm{AN}} = b_1^2/4b_2a_{\mathrm{A}}$. The price one pays in the process of elimination of q_0 is to modify the coupling parameters between S and ψ_0 as well as to renormalise the metastable temperature T^*_{AN}. Since the effective free energy Equation (10) contains coupling between S and ψ_0, T^*_{AN} is expected to become renormalised again due to these couplings. Such a renormalisation of T^*_{AN} can be addressed according to the de Gennes argument [27,31] for the N–S$_{\mathrm{A}}$ transition and the free energy can be written as

$$f \approx f_{\mathrm{N}}(S_0) + \frac{1}{2}f''_{S_0}(S - S_0)^2 + \frac{1}{2}a_{\mathrm{A}}(T - \bar{T}_{\mathrm{AN}})\psi_0^2 + \frac{1}{4}c_{\mathrm{A}}\psi_0^4 + \gamma S\psi_0^2 + \frac{3}{4}\lambda_{\mathrm{eff}}S^2\psi_0^2, \tag{11}$$

where $f_{\mathrm{N}}(S_0)$ is the free energy of the nematic phase and S_0 is the nematic order parameter value at the transition. After minimisation and elimination of S, one finds

$$f \approx f_{\mathrm{N}}(S_0) + \frac{1}{2}a_{\mathrm{A}}(T - T''_{\mathrm{AN}})\psi_0^2 + \frac{1}{4}\tilde{c}_{\mathrm{A}}\psi_0^4 \tag{12}$$

where

$$T''_{\mathrm{AN}} = \bar{T}_{\mathrm{AN}} - \frac{2\gamma}{a_{\mathrm{A}}}S_0 - \frac{3\lambda_{\mathrm{eff}}}{2a_{\mathrm{A}}}S_0^2. \tag{13}$$

Here $\tilde{c}_{\mathrm{A}} = c_{\mathrm{A}} - \gamma^2/f''_{S_0} - 2\gamma\lambda_{\mathrm{eff}}S_0/f''_{S_0}$ and the expressions for $\bar{T}_{\mathrm{AN}}$, γ and λ_{eff} are given earlier.

3. Results and discussion

The above formulation provides a way to renormalise the N–S$_{\mathrm{A}}$ transition temperature in terms of the couplings γ and λ_{eff} and the metastable temperature T'_{AN}, Equation (11), whereas in earlier approaches, the renormalised N–S$_{\mathrm{A}}$ transition temperature is derived in terms of γ only. This was due to the fact that in the low-pressure regime (in order to describe the pressure variation of the N–S$_{\mathrm{A}}$ transition temperature), the pressure dependence was considered only in the parameters e_1 and b_1 and was neglected in b_2. In the formulation of Lelidis and Durand [27], since there was no T'_{AN} (this appears in this work due to the elimination of q_0 from the free energy, Equation(6)), the appearance of the reentrant phenomenon was discussed only in the language of γ and λ_{eff}. The presence of a nematic phase below the smectic phase reappears when a high value of the orientational parameter S disfavours the smectic positional ordering ψ_0. This is represented in their Landau–de Gennes model by the presence of a large and positive coefficient λ_{eff} for the $S^2\psi_0^2$ coupling term in the free energy. For such a case, the smectic line $\psi_0^2 = 0$ is a parabola with $S^{\pm}_{\psi_0=0} = \gamma/3\lambda_{\mathrm{eff}} \pm \sqrt{(\gamma/3\lambda_{\mathrm{eff}})^2 - 2A^*_{\mathrm{A}}/3\lambda_{\mathrm{eff}}}$. For reentrance, the whole parabola defined by $S^{\pm}_{\psi_0=0}$ has a physical meaning when the $\mathrm{S_A}$ phase can exist inside it. In the present case, the above explanation for the reentrant transition still holds except that the parabola $\psi_0^2 = 0$ has to be described by three parameters γ, λ_{eff} and T'_{AN}. Since the reentrant transition is counterintuitive, there can be a general remark in the present situation. Compressing the nematic phase due to an increase in pressure leads to a smectic phase where the decrease in internal energy associated with the formation of layers overcomes the loss in entropy. Compressing the $\mathrm{S_A}$ phase further causes a strong decrease in the internal energy where the free energy of the system has to be minimised at the expense of the increase in entropy. This causes a collapse of the $\mathrm{S_A}$ phase and hence the $\mathrm{N_R}$ phase. At the molecular level, as has already been mentioned in the introduction, the long-range repulsive forces win over the short-range attractive forces, which drives the layers apart and gives rise to the reentrant nematic phase.

It has been observed from the experimental pressure variation of the N–$\mathrm{S_A}$ transition temperature [19] that it increases with increasing pressure. Beyond a critical pressure the transition temperature turns around and the *P*–*T* phase diagram becomes a parabola, which in turn makes the nematic phase reappear. This is what appears as the observed reentrant phenomenon. Moreover, the layer spacing has been measured experimentally using an X-ray diffraction method [22,23] during the reentrant transition. It remains constant with increase in pressure.

From the expressions of the N–$\mathrm{S_A}$ transition temperature, Equation (13), and the 'inverse layer spacing', Equation (7), in addition to the above experimental observations [22,23,25], it is obvious that the coupling parameters e_1, b_1 and b_2 are pressure dependent. This makes the renormalised metastable temperature T'_{AN} and the effective couplings γ and λ_{eff} also pressure dependent. Considering the experimental *P*–*T* phase diagram [25] and the pressure data of q_0 [22,23], we computed the pressure dependence of e_1, b_1 and b_2, and hence T'_{AN}, γ and λ_{eff}, by using the Landau parameters given in Table 1 from [28]. In doing so, we have constrained that such a pressure dependence of the above parameters satisfies the cubic Equation (9) for *S*. The *P* dependence of T'_{AN}, γ and λ_{eff} is shown in Figures 1, 2 and 3. It can be seen that they vary sharply (but continuously) at the critical pressure P_c (~1900 bar) beyond which the $\mathrm{N_R}$ phase reappears. Moreover, a *S*–*T* phase diagram at two different pressures (above and below P_c) has been derived from such a pressure dependence of T'_{AN}, γ and λ_{eff} and the $\psi_0^2 = 0$ line has been shown to form a parabola for $P > P_c$ but not for $P < P_c$. This confirms the appearance of the reentrant phenomenon (Figure 4).

Table 1. Model parameters chosen [28] for the calculation of the phase diagram.

Parameters	Value
a_{N}	0.13×10^7 erg K^{-1} cm^{-3}
b_{N}	-2.46×10^7 erg cm^{-3}
c_{N}	1.11×10^7 erg cm^{-3} erg
a_{A}	0.13×10^7 erg K^{-1} cm^{-3}
c_{A}	0.25×10^7 erg cm^{-3}

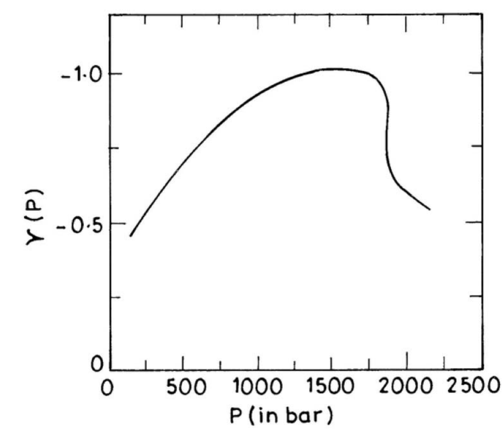

Figure 1. Variation of the coupling parameter γ ($\times\ 10^7$ erg cm^{-3}) as a function of pressure.

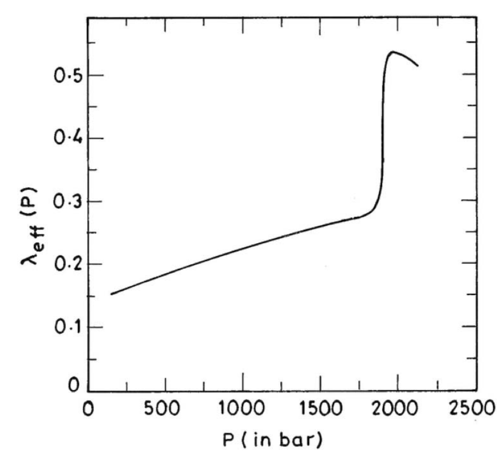

Figure 2. Variation of the coupling parameter λ_{eff} ($\times\ 10^7$ erg cm^{-3}) as a function of pressure.

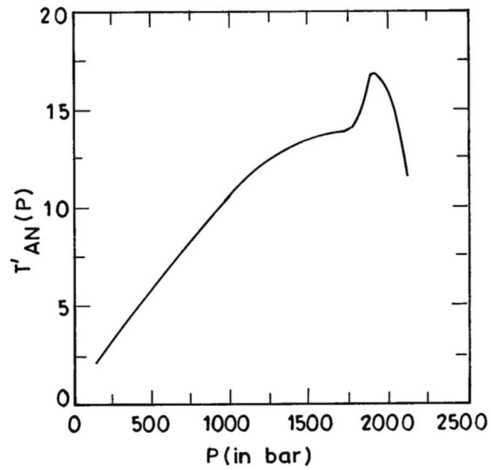

Figure 3. Variation of T'_{AN} (°C) as a function of pressure.

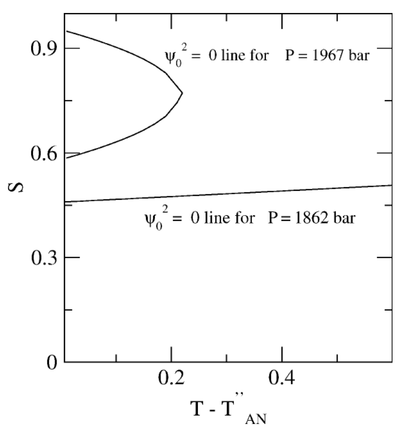

Figure 4. The *S–T* phase diagram where the critical pressure $P_c \sim 1900$ bar.

The present formulation for the reentrant transition in liquid crystals can be contrasted with that of earlier phenomenological theories such as that of Lelidis and Durand [27]. Since in the present case the effect of q_0 fluctuations has been incorporated, the free energy contains terms which have couplings of q_0 to the nematic and smectic order parameters. The elimination of q_0 yields a free energy which is similar to that of Lelidis and Durand [27], except that it gives rise to a metastable temperature which is pressure dependent. Thus one at least needs three pressure-dependent parameters to describe the pressure-driven reentrant phenomena whereas in the case of Lelidis and Durand it is only two. The latter case looks unphysical since the N–S_A transition temperature might not be largely renormalised to give reentrant phenomena by just varying γ and $\lambda_{\rm eff}$, rather T'_{AN} helps one to do so. Moreover, the pressure dependence of the layer thickness makes the metastable temperature pressure dependent. Thus, the present work which is experimentally driven removes the above difficulty and explains the occurrence of the reentrant phenomenon well. Therefore, we believe this to be a more general Landau–de Gennes approach for the reentrant transition in liquid crystals which takes care of q_0 fluctuations in the theory. In a recent computer simulation study [24], the variation of smectic order parameter with respect to packing fraction for different isotherms has shown the existence of a order parameter discontinuity at the transition (critical pressure) and hence a second tricritical point along the S_A–N_R line. We believe that the present work might be associated with such a new tricritical point along S_A–N_R transition which will be discussed in a future publication [32].

4. Summary and conclusions

A thermodynamic model based on Landau–de Gennes theory for the thermodynamic and phase transition properties of achiral mesogenic materials exhibiting the phase sequence I–N–S_A on cooling has been proposed to explain the origin of nematic reentrance observed in high-pressure experimental studies. The free-energy density is written as an expansion series containing terms involving powers of nematic and smectic (S, ψ) order parameters and the (S, ψ) and (S, ψ q_0) coupling terms. The most important feature of the work is that the inverse layer spacing q_0, which mimics an order parameter, becomes coupled to the (S, ψ) order parameters. An effective free-energy density (Equation (10)) is derived by eliminating q_0 from Equation (6). In this process a N–S_A metastable temperature T'_{AN} is defined involving the coefficients a_A, b_1 and b_2. The basic idea is to make γ, $\lambda_{\rm eff}$ and T'_{AN} pressure dependent. We have shown that the nematic reentrance is caused by the pressure dependence of these quantities. Based on a similar phenomenological formulation, Lelidis and Durand [27] studied the phase transitions in achiral mesogens under the application of an electric field and showed that the electric-field-induced transitions can be explained only by the γ and $\lambda_{\rm eff}$ terms in the free energy and that the nematic reentrance occurs due to the large and positive $\lambda_{\rm eff}$ coefficient. In the present work, the role of the inverse layer spacing q_0 has been investigated and it has been observed that the occurrence of nematic reentrance is due to the pressure dependence of the coupling coefficients γ and $\lambda_{\rm eff}$ as well as the N–S_A metastable temperature T'_{AN}. Considering the experimental *P–T* phase diagram [25] and the pressure variation of q_0, the pressure dependence of γ, $\lambda_{\rm eff}$ and T'_{AN} has been computed. We have found that these parameters vary smoothly but rapidly at the critical pressure beyond which the reentrant nematic phase appears. We have evaluated the *S–T* phase diagram at two pressures $P > P_C$ and $P < P_C$ from the pressure dependence of

T'_{AN}, and λ_{eff} and the $\psi_0^2 = 0$ line has been shown to form a parabola for $P > P_C$ but not for $P < P_C$. This provides confirmation of the existence of the reentrant nematic phase for $P \geq P_C$.

Acknowledgements

Financial support from DST, New Delhi is gratefully acknowledged. One of us (Amit Srivastava) is grateful to CSIR, New Delhi for a Senior Research Fellowship.

References

[1] Cladis, P.E. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 85–129; Cladis, P.E. *Liq. Crysts.* **1998**, *24,* 15–19.
[2] Nayeem, A.; Freed, J.H. *J. Phys. Chem.* **1989**, *93*, 6539–6550.
[3] Narayanan, T.; Kumar, A. 1994 *Phys. Rep.* **1994**, *249*, 135–218.
[4] Radzihovsky, L. *Eur. Phys. Lett*. **1996**, *36,* 595–600; Radzihovsky, L. In *Physical Properties of Liquid Crystals*, Demus, D. *et al*., Eds.; Wiley VCH, Weinheim, 1989.
[5] Pociecha, D.; Gorecka, E.; Cepic, M.; Vaupotic, N.; Zeks, B.; Kardas, D.; Mieczkowski *Phys. Rev. Lett.* **2001**, *14*, 3048–3051.
[6] Singh, S. *Liquid Crystal Fundamentals*; World Scientific, 2002; Chapter 5; Singh, S. *Phase Transitions* **2000**, *72*, 183–209.
[7] Yamamoto, S.; Sakai, T.; Koga, A. *J. Phys. Soc. Japan* **2002**, *71*, 1250–1253.
[8] Patel, N.M.; Rosenblatt, C.; Yu, Y. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2003**, *68*, 011703–011707.
[9] Krishnaswamy, R.; Raghunathan, V.A.; Sood, A.K. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2004**, *69*, 031905–031908.
[10] Hetenyi, B.; Scandolo, S.; Tosatti, E. *Phys. Rev. Lett.* **2005**, *94*, 125503–125506.
[11] Simoes, M.; Alves, F.S.; Yamaguti, K.E.; Santoro, P.A.; Kimura, N.M.; Palangana, A.J. *Liq. Cryst.* **2006**, *33*, 99–102.
[12] Seferoglu, N.; Kutlu, B. *Physica A* **2007**, *374*, 165–172.
[13] Braga, W.S.; Kimura, N.M.; Luders, D.D.; Sampaio, A.R.; Santoro, P.A.; Palangana, A.J. *Eur. Phys. J. E* **2007**, *24*, 247–250.
[14] Simoes, M.; Pazetti, M.; Domiciano, S.M.; Oliveira, D.A.; Palangana, A.J. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2008**, *78*, 022702–022705.
[15] Na, Y.; Naruse, Y.; Fukuda, N.; Orihara, H.; Fajav, A.; Hamplova, V.; Kospav, M.; Glogarova, M. *Ferroelectrics* **2008**, *364*, 13–19.
[16] Wang, J.L.; Campbell, S.J.; Zeng, R.; Poh, C.K.; Dou, S.X.; Kennedy, S.J. *J. Appl. Phys.* **2009**, *105*, 07A909–07A911.
[17] Yelamaggad, C.V.; Tamilenthi, V.P.; Shanker Rao, D.S.; Nair, G.G.; Prasad, S.K. *J. Mater. Chem.* **2009**, *19*, 2906–2908.
[18] Cladis, P.E. *Phys. Rev. Lett.* **1975**, *35*, 48–51.
[19] Cladis, P.E.; Bogardus, R.K.; Daniels, W.B. *Phys. Rev. Lett.* **1977**, *39*, 720–723.
[20] Cladis, P.E.; Bogardus, R.K.; Aadsen, D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1978**, *18*, 2292–2306.
[21] Liebert, L.; Daniels, W.B. *J. Physique* **1977**, *38*, L333–L335.
[22] Guillon, D.; Cladis, P.E.; Stamatoff, J. *Phys. Rev. Lett.* **1978**, *41*, 1598–1601.
[23] Guillon, D.; Cladis, P.E.; Aadsen, D.; Daniels, W.B. *Phys. Rev. A: At., Mol., Opt. Phys.* **1980**, *21*, 658–665.
[24] de Miguel, E.; del Rio, E.M. *Phys. Rev. Lett.* **2005**, *95*, 217802–217805.
[25] Cladis, P.E. *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 177–191.
[26] Vaz, N.A.P.; Doane, J.W. *Mol. Cryst. Liq. Cryst.* **1983**, *101*, 35–45.
[27] Lelidis, I; Durand, G. *J. Physique II* **1996**, *6*, 1359–1387.
[28] Srivastava, A.; Sa, D; Singh, S. *Eur. Phys. J. E* **2006**, *20*, 63–69.
[29] Srivastava, A.; Sa, D; Singh, S. *Eur. Phys. J. E* **2007**, *22*, 111–116.
[30] Mukherjee, P.K.; Pleiner, H.; Brand, H.R. *Eur. Phys. J. E* **2001**, *4*, 293–297.
[31] de Gennes P.G. *Mol. Cryst. Liq. Cryst.* **1973** *21*, 49–76.
[32] Srivastava, A.; Sa, D.; Singh, S. Unpublished work, 2009.