

# Effect of magnetic nanoparticles on the nematic-smectic-A phase transition

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## Abstract

Recent experiments on *mixed* liquid crystals have highlighted the hugely significant role of ferromagnetic nanoparticle impurities in defining the nematic-smectic-A phase transition point. Structured around a Flory-Huggins free energy of isotropic mixing and Landau-de Gennes free energy, this article presents a phenomenological mean-field model that quantifies the role of such impurities in analyzing thermodynamic phases, in a mixture of thermotropic smectic liquid crystal and ferromagnetic nanoparticles. First we discuss the impact of ferromagnetic nanoparticles on the isotropic-ferro-nematic and ferro-nematic-ferro-smectic phase transitions and their transition temperatures. This is followed by plotting and discussing various topologies in the phase diagrams. Our model results indicate that there exists a critical concentration of nanoparticle impurities for which the second order N-SmA transition becomes first order at a tricritical point. Calculations based on this model show remarkable agreement with experiment.

Keywords: Liquid crystals; nanoparticles; phase transition

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## I. INTRODUCTION

In recent years, many experiments have found that liquid crystals doped with dispersive materials e.g. carbon nanotubes, silica microbeads, nanoparticles and various collides exhibit remarkable new physical phenomena. Experiments have shown that nanoparticles and ferroelectric nanoparticles can greatly enhance the physical properties of nematic and smectic liquid crystals [1–11].

The mixture of nematic and smectic liquid crystals and magnetic nanoparticles is known as a ferronematic and ferrosmectic. A number of experimental studies [12–25] are devoted to study of ferrosmectic phase in both in thermotropic and lyotropic liquid crystals. The most essential feature of the ferrosmelectics is that their structure aligns parallel to an external magnetic field. Potocova et al. [13] studied the structural instabilities of the ferronematic and ferrosmelectic phases prepared from 8CB ( $\text{CH}_3(\text{CH}_2)_7(\text{C}_6\text{H}_4)_2\text{CN}$ ). Martinez-Miranda et al. [12] studied how the surface coating interacts with the liquid crystal in conjunction with the ferromagnetic nanoparticles (FNP). They have found out that depending on the surface coating the interaction of the ferromagnetic nanoparticles with the liquid crystal varies. Cordoyiannis et al. [14] experimentally studied the impact of magnetic nanoparticles on the isotropic-nematic (I-N) and nematic-Smelectic-A (N-SmA) phase transitions of 8CB. This work shows that the I-N transition remains weakly first order even in the presence of FNP. For the N-SmA phase transition the results of this work show a crossover from anisotropic criticality towards tricriticality. Kopcansky et al. [21, 22] studied the magnetic Freedericksz transition on ferronematics based on the nematic liquid crystal doped with magnetic particles of different size and volume concentration. Zakerhamidi et al. [23] studied the dielectric properties of nematic and ferronematic liquid crystals doped with ferromagnetic nanoparticles. Shuai et al. [25] studied a fluid suspension of magnetic nanoplates that spontaneously aligns into an equilibrium nematic liquid crystal phase.

A large number of theoretical works [26–34] have been carried out to describe the effect of anisotropic nanoparticles, carbon nanotubes and ferroelectric nanoparticles in nematic and smectic liquid crystals. However, very few or practically no theoretical work has been attempted to explain the phase behavior of the N-SmA phase transition in thermotropic liquid crystals (TLC) in the mixture of FNP. Gorkunov et al. [31] studied the effect of nanoparticles embedded in nematic liquid crystals on the nematic-isotropic phase transition based on mean-field theory. They showed that spherically isotropic nanoparticles effectively dilute the liquid crystal medium and decrease the nematic-isotropic transition temperature. Raikher et al. [32] developed a mean-field theory to describe the effect ferromagnetic nanoparticles on the nematic-isotropic phase transition. It

was observed that depending on the anchoring conditions on the particle surface, the particles might either enhance or decrease the clearing temperature of the suspension. In such a suspension, often termed ferronematic, the ability of the particles to be aligned by the magnetic field results in occurrence of a partially oriented (paranematic) state above the transition temperature. Only one theoretical work [35] on ferrosmectic phase in LLC is available in the literature but that is not quantitatively explicit either. Thus it is interesting to see how the ferromagnetic nanoparticles influence the character of the N-SmA phase transition in TLC. Based on this core question, here we to develop a phenomenological model structured around the Flory-Huggins theory [36] to discuss the I-N and N-SmA phase transitions in the in the mixture of FNP.

## II. MODEL

In this section, we use the combination of Flory-Huggins theory and Landau-de Gennes theory for the binary mixture of calamitic SmA liquid crystal and ferromagnetic nanoparticles. First we describe the order parameters necessary in the model free energy. The smectic-A phase has both the orientational and translational ordering. The nematic order parameter, originally proposed by de Gennes [37], is a symmetric, traceless tensor described by  $Q_{ij} = \frac{S}{2}(3n_i n_j - \delta_{ij})$ , where  $n_i$  are unit vectors specifying the preferred orientation of the primary molecular axes, also called directors. The quantity  $S$  defines the strength of the nematic ordering. The layering in the SmA phase is characterized [37] by the order parameter  $\psi(\mathbf{r}) = \psi_0 \exp(-\mathbf{i}\Psi)$ , which is a complex scalar quantity whose modulus  $\psi_0$  is defined as the amplitude of a one dimensional density wave characterized by the phase  $\Psi$ . The magnetic order is described by the magnetization  $\mathbf{M} = M\hat{\mathbf{m}}$  such that  $|M| = 0$  in paramagnetic state and  $|M| \neq 0$  in the ferromagnetic state. Thus we use  $Q_{ij}$ ,  $\psi$ , and  $\mathbf{M}$  as order parameters necessary for the description of the I-N and N-SmA phase transitions in the mixture of FNP.

The total free energy per unit volume of the mixture can be written as

$$f = f_{\text{mix}} + f_{NP} + F_{LC} + f_{\text{int}}, \quad (2.1)$$

where  $f_{\text{mix}}$  is the free energy mixing of isotropic liquids;  $f_{NP}$  describes the contribution of the FNP dispersed in liquid crystal,  $F_{LC}$  represents the free energy of SmA ordering of liquid crystals and  $f_{\text{int}}$  describes the coupling between FNP and SmA ordering, respectively.

The isotropic mixing free energy density may be approximated in terms of the Flory-Huggins

theory [36]

$$\frac{f_{\text{mix}}}{k_B T} = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) + \frac{\lambda}{2} (\nabla \phi)^2, \quad (2.2)$$

where  $k_B$  is the Boltzmann constant and  $T$  is absolute temperature.  $\phi$  and  $(1 - \phi)$  describe the volume fractions of FNP and SmA liquid crystals.  $\frac{\lambda}{2} (\nabla \phi)^2$  is the Ginzburg-Landau term. Here  $\phi = N_{NP} v_{NP} / V$ .  $v_{NP} = \frac{4}{3} \pi R_{NP}^3$ , where  $R_{NP}$  is radius of the nanoparticle.  $\chi$  is a temperature-dependent function which can be defined as  $\chi = A + \frac{B}{T}$  is known as the Flory-Huggins interaction parameter with  $A$  and  $B$  are constants.

The contribution of the FNP free energy density can be expressed as

$$f_{NP} = \phi \left[ \frac{1}{2} p \mathbf{M}^2 + \frac{1}{4} q \mathbf{M}^4 \right] \quad (2.3)$$

The material parameter  $p$  can be assumed as  $p = p_0(T - T_3^*)$ .  $p_0$  is a positive constant and  $T_3^*$  is the virtual transition temperature. We assume  $q > 0$  for the stability of the free energy.

The SmA free energy density can be expressed as

$$f_{LC} = (1 - \phi) \left[ \frac{1}{3} a Q_{ij} Q_{ij} - \frac{4}{9} b Q_{ij} Q_{jk} Q_{ki} + \frac{1}{9} c (Q_{ij} Q_{ij})^2 + \frac{1}{3} L \nabla_i Q_{jk} \nabla_i Q_{jk} + \frac{1}{2} \alpha |\psi|^2 + \frac{1}{4} \beta |\psi|^4 - \frac{1}{2} \delta_{ij} Q_{ij} |\psi|^2 + \frac{1}{2} d_1 |\nabla_i \psi|^2 \right] \quad (2.4)$$

$a$  and  $\alpha$  can be assumed as  $a = a_0(T - T_1^*)/T_1^*$  and  $\alpha = \alpha_0(T - T_2^*)/T_2^*$ ,  $a_0 > 0$  and  $\alpha_0 > 0$ .  $T_1^*$  and  $T_2^*$  are the virtual transition temperatures. We choose  $c > 0$ ,  $b > 0$  and  $\beta > 0$  for the stability of the free energy density (2.4). Here  $\delta_j = \delta n_i n_j$ . The coupling constant  $\delta$  is chosen positive to favor the smectic-A phase over the nematic phases.  $L$  and  $d_1$  are the orientational and translational elastic constants.

The contribution to free energy density due the interactions is written as

$$f_{\text{int}} = -\phi(1 - \phi) \left[ \frac{1}{2} \gamma M_i M_j Q_{ij} + \frac{1}{3} \eta_1 \mathbf{M}^2 Q_{ij} Q_{ij} + \frac{1}{2} \eta_2 M_i M_k Q_{ij} Q_{kj} + \frac{1}{2} \omega \mathbf{M}^2 |\psi|^2 \right] \quad (2.5)$$

The parameters  $\gamma$ ,  $\eta_{1,2}$ , and  $\omega$  are coupling constants. The positive values of  $\gamma$ ,  $\eta_{1,2}$ , and  $\omega$  ensures the ferromagnetic order induced by the nematic order and translational order. Equations (2.2)-(2.5) are all tacitly structured around the standard symmetricity argument.

Following Pleiner et al. [38] we consider the ordering directions between  $\hat{\mathbf{n}}$  and  $\hat{\mathbf{m}}$  make an angle  $\theta_f$  i.e.  $\hat{\mathbf{n}} \cdot \hat{\mathbf{m}} = \cos \theta_f$ . Now we consider the phases in which the smectic order parameter and nematic order parameters are spatially homogeneous, i.e.  $\psi = \text{const}$  and  $S = \text{const}$  for the simplicity of the calculation. Then the total free energy density (2.1) leads to

$$f = k_B T \left[ \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) + \frac{\lambda}{2} (\nabla \phi)^2 \right]$$

$$\begin{aligned}
& +(1-\phi) \left[ \frac{1}{2}aS^2 - \frac{1}{3}bS^3 + \frac{1}{4}cS^4 + \frac{1}{2}\alpha\psi_0^2 + \frac{1}{4}\beta\psi_0^4 - \frac{1}{2}\delta\psi_0^2S \right] + \phi \left[ \frac{1}{2}pM^2 + \frac{1}{4}qM^4 \right] \\
& -\phi(1-\phi) \left[ \frac{1}{4}\gamma M^2S(3\cos^2\theta_f - 1) + \frac{1}{2}\eta_1 M^2S^2 + \frac{1}{8}\eta_2 M^2S^2(3\cos^2\theta_f + 1) \right. \\
& \left. + \frac{1}{2}\omega M^2\psi_0^2 \right]
\end{aligned} \tag{2.6}$$

Minimization of Eq. (2.6) with respect to  $S$ ,  $\psi_0$ ,  $M$  and  $\theta_f$  yields the following five stable solutions excluding the ferromagnetic state:

- (I) Isotropic phase (I):  $S = 0$ ,  $\psi_0 = 0$ ,  $M = 0$ ,  $\theta_f = 0$ . This phase exists for  $a > 0$ ,  $\alpha > 0$ , and  $p > 0$ .
- (II) Nematic phase (N):  $S \neq 0$ ,  $M = 0$ ,  $\psi_0 = 0$ ,  $\theta_f = 0$ . This phase exists for  $a < 0$ ,  $\alpha - \delta S > 0$ ,  $p - (1 - \phi)\gamma'S - (1 - \phi)\eta'S^2 > 0$ .
- (III) Smectic-A phase (SmA):  $S \neq 0$ ,  $\psi_0 \neq 0$ ,  $M = 0$ ,  $\theta_f = 0$ .  
This phase exists for  $a < 0$ ,  $\alpha - \delta S < 0$ , and  $p - (1 - \phi)\gamma'S - (1 - \phi)\eta'S^2 + \omega\psi_0^2 > 0$ .
- (IV) Ferronematic phase (FN):  $S \neq 0$ ,  $\psi_0 = 0$ ,  $M \neq 0$ ,  $\theta_f = 0$  or  $\theta_f = \frac{\pi}{2}$ . This phase exists for  $a < 0$ ,  $p - (1 - \phi)\gamma'S - (1 - \phi)\eta'S^2 < 0$ ,  $\alpha - \delta S > 0$ .
- (V) Ferrosmectic phase (FSmA):  $S \neq 0$ ,  $\psi_0 \neq 0$ ,  $M \neq 0$ ,  $\theta_f = 0$  or  $\theta_f = \frac{\pi}{2}$ . This phase exists for  $a < 0$ ,  $p - (1 - \phi)\gamma'S - (1 - \phi)\eta'S^2 + \omega\psi_0^2 < 0$ ,  $\alpha - \delta S < 0$ .

In the description above, we have used  $\eta' = \eta_1 + \frac{\eta_2}{4}(3\cos^2\theta_f + 1)$  and  $\gamma' = \frac{1}{2}(3\cos^2\theta_f - 1)\gamma$ . For the specific cases in hand,  $\gamma' = \gamma(or - \frac{\gamma}{2})$  for  $\theta_f = 0$  (or  $\frac{\pi}{2}$ ) and  $\eta' = (\eta_1 + \eta_2)$  (or  $(\eta_1 + \eta_2/2)$ ) for  $\theta_f = 0$  (or  $\frac{\pi}{2}$ ).

The necessary conditions for the four different liquid crystalline phases to be stable (Hessian determinant) are given below:

$$\begin{aligned}
\frac{\partial^2 f}{\partial S^2} > 0, \quad \frac{\partial^2 f}{\partial M^2} > 0, \quad \frac{\partial^2 f}{\partial \psi_0^2} > 0, \\
\frac{\partial^2 f}{\partial u^2} \cdot \frac{\partial^2 f}{\partial v^2} - \left( \frac{\partial^2 f}{\partial u \partial v} \right)^2 > 0,
\end{aligned}$$

where  $u, v \in \{S, \psi_0, M\}$ .

Now it is clear from the above solutions that I-N, I-SmA, I-FN, I-FSmA, N-SmA, N-FN, N-FSmA, FN-FSmA, FN-SmA, SmA-FSmA phase transitions are possible. I-N, I-SmA, I-FN, I-FSmA phase transitions must always be first order because of the cubic invariant  $b$  in the free energy

expansion (2.6). Other phase transitions can be first or second order depending on the concentration of FNP. In the following we will discuss only the I-FN and FN-FSmA phase transitions which is observed experimentally.

### A. I-FN phase transition

The free energy density near the I-FN phase transition can be expressed as

$$\begin{aligned}
f = k_B T & \left[ \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) + \frac{\lambda}{2} (\nabla \phi)^2 \right] \\
& + (1 - \phi) \left[ \frac{1}{2} a S^2 - \frac{1}{3} b S^3 + \frac{1}{4} c S^4 \right] + \phi \left[ \frac{1}{2} p M^2 + \frac{1}{4} q M^4 \right] \\
& - \phi(1 - \phi) \left[ \frac{1}{2} \gamma' M^2 S + \frac{1}{2} \eta' M^2 S^2 \right]
\end{aligned} \tag{2.7}$$

The value of the magnetization in the FN phase can be expressed as

$$M^2 = -\frac{1}{q} (p - (1 - \phi)(\gamma' S + \eta' S^2)), \tag{2.8}$$

The substitution of  $M$  from Eq. (2.8) into Eq. (2.7), we get

$$\begin{aligned}
f_{NA} = k_B T & \left[ \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) + \frac{\lambda}{2} (\nabla \phi)^2 \right] \\
& + (1 - \phi) \left[ \phi \frac{p\gamma'}{2q} S + \frac{1}{2} a^* S^2 - \frac{1}{3} b^* S^3 + \frac{1}{4} c^* S^4 \right]
\end{aligned} \tag{2.9}$$

$$a^* = a - \phi(1 - \phi) \frac{\gamma'^2}{2q} + \phi \frac{p\eta'}{q}, \quad b^* = b + \phi(1 - \phi) \frac{3\gamma'\eta'}{2q}, \quad c^* = c - \phi(1 - \phi) \frac{\eta'^2}{q}.$$

The renormalized coefficients show that the Landau coefficients  $a^*$ ,  $b^*$  and  $c^*$  change with change of the concentration of FNP.

In order to ensure the stability of the FN phase, we require

$$a^* - 2b^* S + 3c^* S^2 > 0, \tag{2.10}$$

$$p - (1 - \phi)(\gamma' S + \eta' S^2) < 0, \tag{2.11}$$

$$a_1 - 2b_1 S + 3c_1 S^2 > 0, \tag{2.12}$$

where

$$a_1 = a^* - \phi(1 - \phi) \frac{\gamma'^2}{2q}, \quad b_1 = b^* + \phi(1 - \phi) \frac{\gamma'\eta'}{q}, \quad c_1 = c^* - \phi(1 - \phi) \frac{2\eta'^2}{3q}.$$

Now the value of  $S$  in the FN phase can be calculated from the equations

$$\phi \frac{p\gamma'}{2q} + a^* S - b^* S^2 + c^* S^3 = 0 \tag{2.13}$$

The temperature variation of the order parameter ( $S$ ) for pure sample and a fixed concentration of FNP in the FN phase is shown in Fig.1. This is done for a set of phenomenological parameters for which the direct I-N and I-FN phase transitions are possible. Figure 1 shows that I-FN transition temperature and the jump of the order parameter  $S$  decrease with the increase of the concentration of FNP. For a fixed set of parameter values, we find for pure sample  $S_{I-N} = 0.48$ . For the volume fraction  $\phi = 0.02$ , we find  $S_{I-FN} = 0.46$ . The low value of  $S_{I-FN}$  indicates the weakly first order character of the I-FN phase transition. Thus the I-FN transition is still a weakly first order transition even in the mixture of FNP. The present analysis completely agree with experimental results of Cordoyiannis et al. [14].

The free energy density (2.9) describes the I-FN phase transition. At the dimensional level, the Ginzburg-Landau free energy term  $[\frac{\lambda}{2}(\nabla\phi)^2]$  effectively renormalizes the value of the parameter  $\chi$  by rescaling the quadratic  $\phi^2$ -term with a  $\frac{\lambda}{L^2}$  type term, where  $L$  is the typical scaling length of the system. Beyond the mean-field level, the  $\frac{1}{L^2}$ -dependence will further renormalize the spatial correlation function. The cubic coefficient  $b^*$  in the free energy density (2.9) shows that the I-FN phase transition must always be first order in mean field approximation. Lower the value of  $b^*$ , weakly the first order character of the I-FN phase transition.

The conditions for the first order I-FN phase transition can be obtained as

$$f_{FN}(S) = F_0(T), f'_{FN}(S) = 0, f''_{FN}(S) \geq 0 \quad (2.14)$$

The conditions for phase equilibrium require that the chemical potentials in the isotropic and FN phases are equivalent i.e  $\mu_{iso} = \mu_{FN}$ .

The FN phase appears only for  $a^* < 0$  i.e.

$$T < T_{I-FN}^* + \frac{\phi(1-\phi)\gamma'^2 T_2^*}{2qa_0^*} \quad (2.15)$$

where  $T_{I-FN}^* = \frac{a_0 T_1^* + \frac{\phi\eta' p_0 T_f T_1^*}{q}}{a_0^*}$ ,  
 $a_0^* = a_0 + \frac{\phi\eta' p_0 T_2^*}{q}$ .

From Eq. (2.15) we observe the decrease of the I-FN transition temperature with the increase of the concentration of FNP as

$$\Delta T_{I-FN} = T_1^* \left( \frac{\phi(1-\phi)\gamma'^2}{2qa_0^*} \right) \quad (2.16)$$

## B. FN-FSmA phase transition

We now discuss the FN-FSmA phase transition.  $S \neq 0$ ,  $\psi_0 \neq 0$ ,  $M \neq 0$ ,  $\theta_f = 0$  or  $\theta_f = \frac{\pi}{2}$  is the stable solution for the FSmA phase. Thus the free energy density (2.6) with  $\theta_f = 0$  or  $\theta_f = \frac{\pi}{2}$  describes the FN-FSmA phase transition.

The values of the smectic ordering and the magnetization in the FSmA phase can be expressed as

$$\psi_0^2 = -\frac{1}{\beta^*} \left( \alpha^* - \delta^* S - \frac{\phi(1-\phi)\omega\eta'}{q} S^2 \right), \quad (2.17)$$

$$M^2 = -\frac{1}{q} \left( p^* - (1-\phi)(\gamma^* S + \eta^* S^2) \right). \quad (2.18)$$

where  $\alpha^* = \alpha + \frac{\phi\omega p}{q}$ ,  $\delta^* = \delta + \frac{\phi(1-\phi)\omega\gamma'}{q}$ ,  $\beta^* = \beta - \frac{\phi(1-\phi)\omega^2}{q}$ ,  $p^* = p + \frac{(1-\phi)\omega\alpha^*}{\beta^*}$ ,  $\eta^* = \eta' + \frac{\phi(1-\phi)\omega\eta'}{q\beta^*}$ ,  $\gamma^* = \gamma' + \frac{\omega\delta^*}{\beta^*}$ .

The above renormalized coefficients show that the interaction parameters  $\delta$ ,  $\eta'$  and  $\gamma'$  change with the change of the concentration of FNP.

It is clear from Eq. (2.17) and Eq. (2.18) that a nonzero real value of  $\psi_0$  and  $M$  exist only when  $\alpha^* - \delta^* S - \frac{\phi(1-\phi)\omega\eta'}{q} S^2 < 0$  and  $p^* - (1-\phi)(\gamma^* S + \eta^* S^2) < 0$ . Since there is a small temperature range where  $\alpha > 0$ ,  $\delta > 0$ ,  $\gamma' > 0$  and  $\eta' < 0$  in this region.

The substitution of  $\psi_0$  and  $M$  from Eqs. (2.17) and (2.18) into Eq. (2.6) gives

$$\begin{aligned} f_{FSmA} = & k_B T \left[ \phi \ln \phi + (1-\phi) \ln(1-\phi) + \chi \phi \left( 1 - \frac{\lambda}{2L^2} \phi \right) \right] \\ & + (1-\phi) \left[ \frac{\delta\alpha^*}{2\beta^*} S + \frac{\phi\gamma'p^*}{2q} S + \frac{1}{2} a^{**} S^2 - \frac{1}{3} b^{**} S^3 + \frac{1}{4} c^{**} S^4 \right] \end{aligned} \quad (2.19)$$

where  $a^{**} = a - \frac{\delta\delta^*}{2\beta^*} - \frac{\phi(1-\phi)\gamma^*\gamma'}{2q} + \frac{\phi\eta'p^*}{q}$ ,  $b^{**} = b + \frac{\phi(1-\phi)\delta\omega\eta'}{2q\beta^*} + \frac{\phi(1-\phi)\gamma^*\eta'}{q} + \frac{\phi(1-\phi)\gamma'\eta^*}{q}$ ,  $c^{**} = c - \frac{\phi(1-\phi)\eta'\eta^*}{q}$ .

The free energy density (2.19) describes the FN-FSmA phase transition. The cubic coefficient  $b^{**}$  in the free energy density (2.5) shows that the FN-FSmA phase transition must be first order in mean field approximation in the mixture of FNP.

The value of  $S$  in the FSmA phase can be calculated from the equation

$$\frac{\delta\alpha^*}{2\beta^*} + \frac{\phi\gamma'p^*}{2q} + a^{**} S - b^{**} S^2 + c^{**} S^3 = 0. \quad (2.20)$$

Equation (2.20) is a cubic equation that admits of an exact solution (Cardano's method) involving the parameters involved.



In order to ensure the stability of the FSmA phase we require

$$a^{**} - 2b^{**}S + 3c^{**}S^2 > 0, \quad (2.21)$$

$$\alpha^* - \delta^*S - \frac{\phi(1-\phi)\omega\eta'}{q}S^2 < 0, \quad (2.22)$$

$$p^* - (1-\phi)\gamma^*S - (1-\phi)\eta^*S^2 < 0. \quad (2.23)$$

$$a_2 - 2b_2S + 2c_2S^2 > 0, \quad (2.24)$$

$$\omega < \sqrt{q\beta/\phi(1-\phi)} \quad (2.25)$$

where  $a_2 = a^{**} - \frac{\phi(1-\phi)\gamma'^2}{2q}$ ,  $b_2 = b^{**} + \frac{\phi(1-\phi)\gamma'\eta'}{q}$ ,  $c_2 = c^{**} - \frac{\phi(1-\phi)2\eta'^2}{3q}$ .

Now The temperature variations of the order parameters ( $S$  and  $\psi_0$ ) for  $\phi = 0$  in the FSmA phase are shown in Fig.2 and Fig.3 respectively for  $\theta_f = 0, \pi/2$ . Figures 4 and 5 show the temperature variations of the same order parameters at the first order FN-FSmA transition point with the change of the concentration of FNP for  $\phi \neq 0$  ( $= 0.02$ ). Figures 4 and 5 show discontinuous phase transitions, as expected.

For threshold temperatures  $T_1 = T_2 = 10$  (in non-dimensionalized units), we find continuous (second order) phase transition for the parameter values  $\theta_f = 0.0$  and  $\phi = 0.0$  (Fig.2 and Fig.3). However, changing the parameter values to  $\theta_f = \pi/2$  and  $\phi = 0$  or  $\phi = 0.02$  (Fig.4 and Fig.5), we find discontinuous jumps, confirming our prediction of a first order phase transition.

The figures above have been drawn using the parameter values  $a_0 = 0.012$ ,  $b = 0.44$ ,  $c = 1.56$ ,  $\alpha_0 = 0.012$ ,  $p = 0.1$ ,  $q = 2.0$ ,  $\beta = 2.07$ ,  $\gamma' = 2.98$ ,  $\eta' = -0.82$ ,  $\delta = 1.01$  and  $\omega = 0.72$ . The coefficients (parameters) entering the Landau free energy are arbitrary and can at best be fitted to the experimental data so as to give the observed physical behavior. Since enough experimental data are not available in the literature, we cannot provide precise quantitative comparison of the values of the coefficients used here against known experimental benchmark. Hence, we have restricted ourselves to parametric windows that portray the physically relevant behavior, focusing on the phase transition aspect. Our choice of parameter values have been guided by the constraint of eliciting continuous variations of  $S$  and  $\psi_0^2$  against  $T$  for  $\phi = 0$  (second order) while showing a discontinuous variation for  $\phi \neq 0$  (first order). Generally, all we can say here is that the values of  $\gamma', \omega > 0$  while  $\eta' < 0$ .

The conditions for the first order FN-FSmA phase transition are given by

$$f_{FSmA}(S) = f_{FN}(S), f'_{FSmA}(S) = 0, f''_{FSmA}(S) \geq 0 \quad (2.26)$$

The conditions for the second order phase N-SmA transition read

$$\alpha^* - \delta^* S - \frac{\phi(1-\phi)\omega\eta'}{q} S^2 = 0, f'_{FN}(S) = 0, f''_{FSmA}(S) \geq 0 \quad (2.27)$$

Again the conditions for phase equilibrium require that the chemical potentials in the FN and FSmA phases are equivalent i.e  $\mu_{FN} = \mu_{FSmA}$ .

The  $\phi$  versus temperature  $T$  variation in the near the FN-FSmA second order phase transition obtained from a self-consistent solution of Eq. (2.27), is shown in Fig.6. The results are shown over a range of values of  $S$ , including the phase transition value  $S \sim 0.3$ , as previously demonstrated in Figs. 2-5. Apart from the generic decaying trend, the results remain largely unaffected by changes in  $\theta_f$  values.

### III. TRICRITICAL BEHAVIOR OF THE FN-FSMA PHASE TRANSITION

In this section we discuss the tricritical behavior of the FN-FSmA phase transition under the influence of FNP. Assume  $S_0$  is the order parameter of the FN phase at the FN-FSmA transition point and  $f_{FN}(S_0)$  is the corresponding free energy density at the FN phase. Then the free energy density for a mixture of liquid crystal and FNP near the FN-FSmA phase transition can be written as

$$f = (1-\phi)(f_{FN}(S_0) + \frac{1}{2}u(S-S_0)^2 + \frac{1}{2}\alpha\psi_0^2 + \frac{1}{4}\beta\psi_0^4 - \frac{1}{2}\delta\psi_0^S) + \phi(\frac{1}{2}pM^2 + \frac{1}{4}qM^4) - \phi(1-\phi)\left(\frac{1}{4}\gamma'M^2S + \frac{1}{2}\eta'M^2S^2 + \frac{1}{2}\omega M^2\psi_0^2\right) \quad (3.1)$$

where  $F_{FN}(S_0)$  is the corresponding free energy density of the FN phase and  $u = 1/\chi_1$ ,  $\chi_1 = (\partial^2 f/\partial S^2)^{-1}$  is the response function near the I-FN transition.

After eliminating the values of  $S$  and  $M$  from Eq. (3.1), we get the free energy density as

$$F = F_{FN}^*(S_0) + \frac{1}{2}\alpha^{**}\psi_0^2 + \frac{1}{4}\beta^{**}\psi_0^4 \quad (3.2)$$

The renormalized coefficients are

$$\begin{aligned} F_{FN}^*(S_0) &= F_{FN}(S_0) - \frac{p^{**2}}{4q^*}, \\ \alpha^{**} &= \alpha - \delta S_0 - \phi \frac{p^{**}\omega^*}{q^*}, \\ \beta^{**} &= \beta - \frac{\delta^2}{2u} - \phi(1-\phi) \frac{\omega^{*2}}{q^*}, \end{aligned}$$

$$\begin{aligned}
p^{**} &= p + \phi(1 - \phi)\frac{\gamma'^2}{4u} - (1 - \phi)\gamma'S_0 - (1 - \phi)\eta'S_0^2, \\
q^* &= q - \phi(1 - \phi)\frac{\gamma'^2}{u} - \phi(1 - \phi)\frac{2\eta'^2}{u}S_0^2 - \phi(1 - \phi)\frac{\eta'\gamma'}{u}S_0, \\
\omega^* &= \omega + \frac{\delta}{u}(\eta'S_0 + \gamma').
\end{aligned}$$

It is clear from the renormalized coefficients that the parameters  $\alpha^{**}$  and  $\beta^{**}$  change with the change of concentration  $\phi$  which indicates change of the order of the FN-FSmA phase transition. For pure 8CB or low value of the concentration  $\phi$  of FNP,  $\beta^{**} > 0$ , then a second order transition occurs.

Then renormalization of the second order FN-FSmA transition temperature can be written as

$$T_{NA}^C = T_{FN-FSmA}^* - \frac{\delta S_0 T_2^*}{\alpha_0^*} - \frac{\omega^* T_2^*}{q^* \alpha_0^*} \phi \left( \frac{\gamma'^2}{4u} - (1 - \phi)\gamma'S_0 + (1 - \phi)\eta'S_0^2 \right) \quad (3.3)$$

where

$$\begin{aligned}
\text{where } T_{FN-FSmA}^* &= \frac{\alpha_0 T_2^* + \frac{p_0 \omega^* T_f T_2^* \phi}{q^*}}{\alpha_0^*}, \\
\alpha_0^* &= \alpha_0 + \frac{\phi \omega^* p_0 T_2^*}{q^*}.
\end{aligned}$$

For the higher value of concentration  $\phi$  of the FNP,  $\beta^{**} < 0$ , the FN-FSmA phase transition is a first order transition. In this case both the N and SmA phases can coexist i.e. a two phase region appears. In this case sixth order term  $\frac{\epsilon}{6}\phi_0^6$  should be added into the free energy density (3.2). Then for the first order FN-FSmA phase transition, the FN-FSmA transition temperature is

$$T_{FN-FSmA} = T_2^* T_{FN-FSmA}^* + \frac{3\beta^{**2} T_2^*}{16e\alpha_0^*} - \frac{\delta S_0 T_2^*}{\alpha_0^*} - \frac{\omega^* T + 2^*}{q^* \alpha_0^*} \phi \left( \frac{\gamma'^2}{4u} - (1 - \phi)\gamma'S_0 + (1 - \phi)\eta'S_0^2 \right) \quad (3.4)$$

Equations (3.3) and (3.4) show that the FN-FSmA transition temperature decreases with increase of the concentration of FNP. This prediction confirms the experimental results [14].

For a tricritical value of the concentration  $\phi_{tcp}$ ,  $\beta^{**} = 0$ , then a tricritical point is obtained. Hence a TCP is achieved with the change of concentration of the FNP.

#### IV. CONCLUSIONS

We have developed a phenomenological model combining with Flory-Huggins theory to describe the effect of ferromagnetic nanoparticles on the I-N and N-SmA phase transitions. The I-FN transition is still a weakly first order transition even in the mixture of FNP. The FN-FSmA transition may be first order. In a binary mixture, the N-SmA transition which is second order only in one of the pure forms, becomes first order with the change of concentration of the FNP. This leads to a crossover from second to first order transition via TCP. Furthermore, both the I-FN and FN-FSmA

transition temperatures decrease with the increase of the concentration of the FNP. We discuss our analysis by plotting various topology of the phase diagram under different conditions. Our results are in qualitative agreement with the experimental results. Our results are expected to encourage further experiments on the impact of FNP on other liquid crystalline phase transitions to verify the validity of the present theory.

In the present work we have discarded spatial variations in the order parameter in our calculation. The inclusion of these derivative terms will give additional physics into these phase transitions. A consideration of spatial variations will also need to be accompanied with spatiotemporal correlations that are likely to alter the critical exponents (not calculated here) at the second epsilon-expansion level. We intend to deal with this problem in the forthcoming paper.

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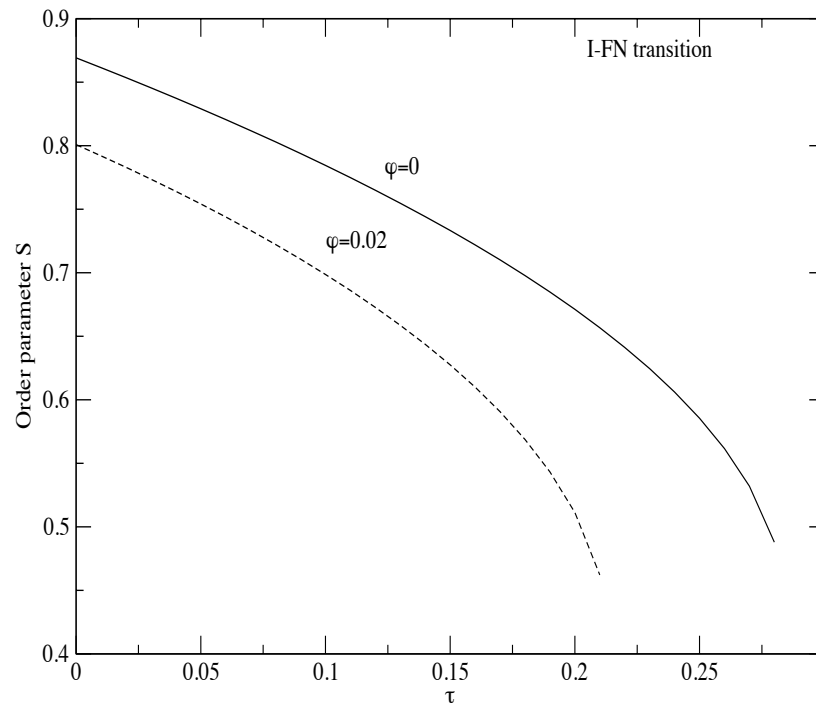


FIG. 1: Order parameter  $S$  varying against the reduced temperature  $t = (T - T_1^*)/T_1^*$  in the FN phase for different concentration of FNP.

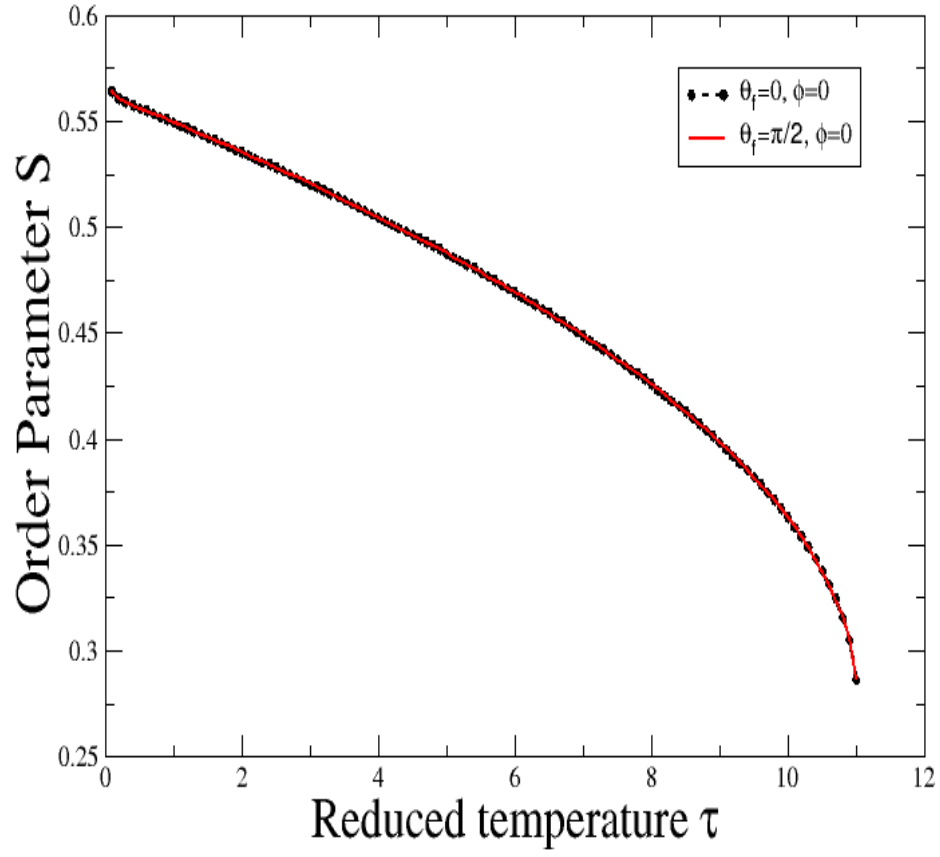


FIG. 2:  $S$  plotted against reduced temperature  $\tau = (T - T_2^*)/T_2^*$ ; plots show continuous decaying trend for  $\phi = 0$  with no dependence on  $\theta_f$  values.

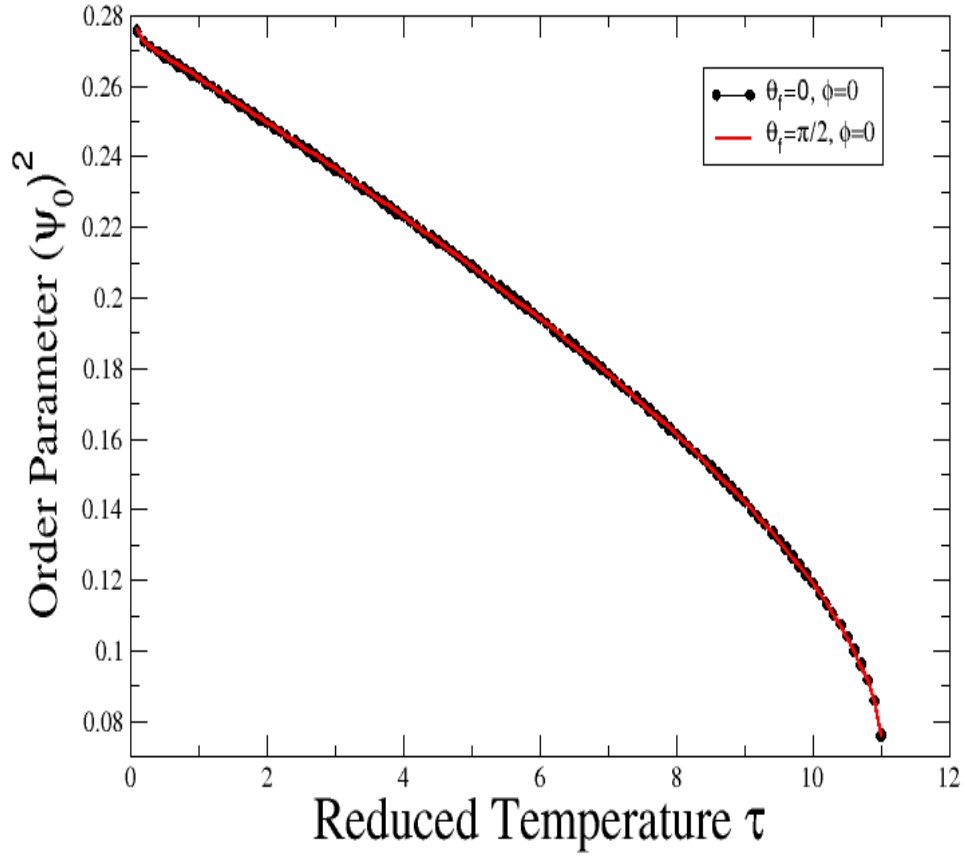


FIG. 3:  $\psi_0^2$  plotted against reduced temperature  $\tau = (T - T_2^*)/T_2^*$ ; plots show continuous decaying trend for  $\phi = 0$  with no dependence on the  $\theta_f$  values.



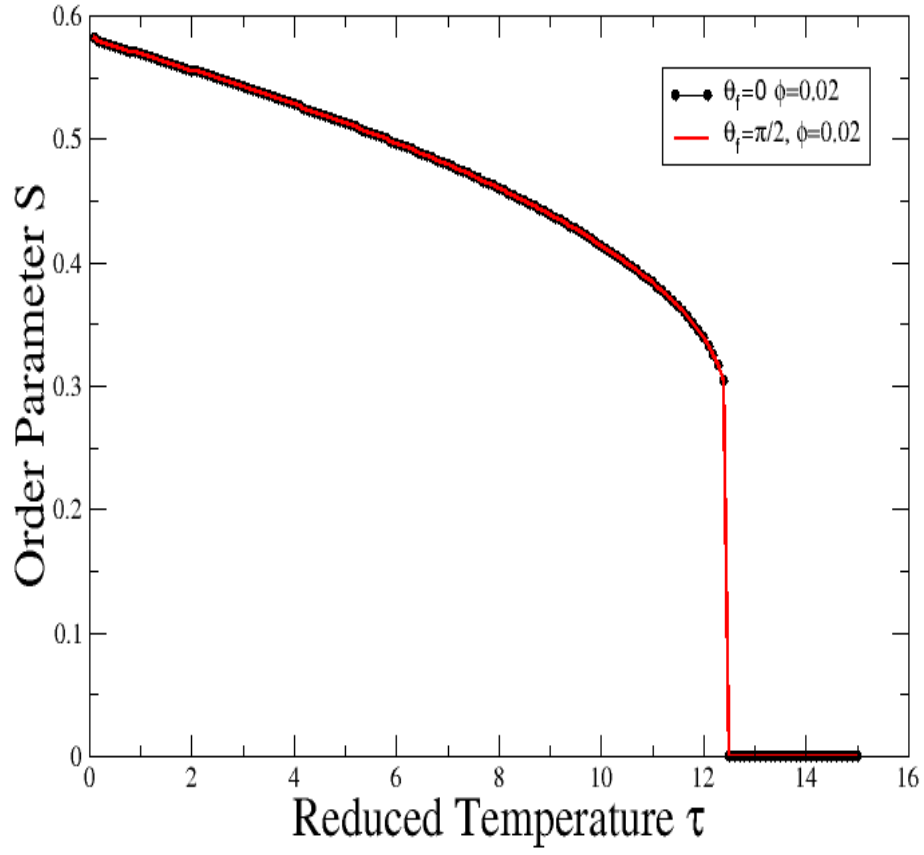


FIG. 4:  $S$  plotted against reduced temperature  $\tau = (T - T_2^*)/T_2^*$ ; plots show discontinuous jump for  $\phi = 0.02$ , independent of  $\theta_f$  values.

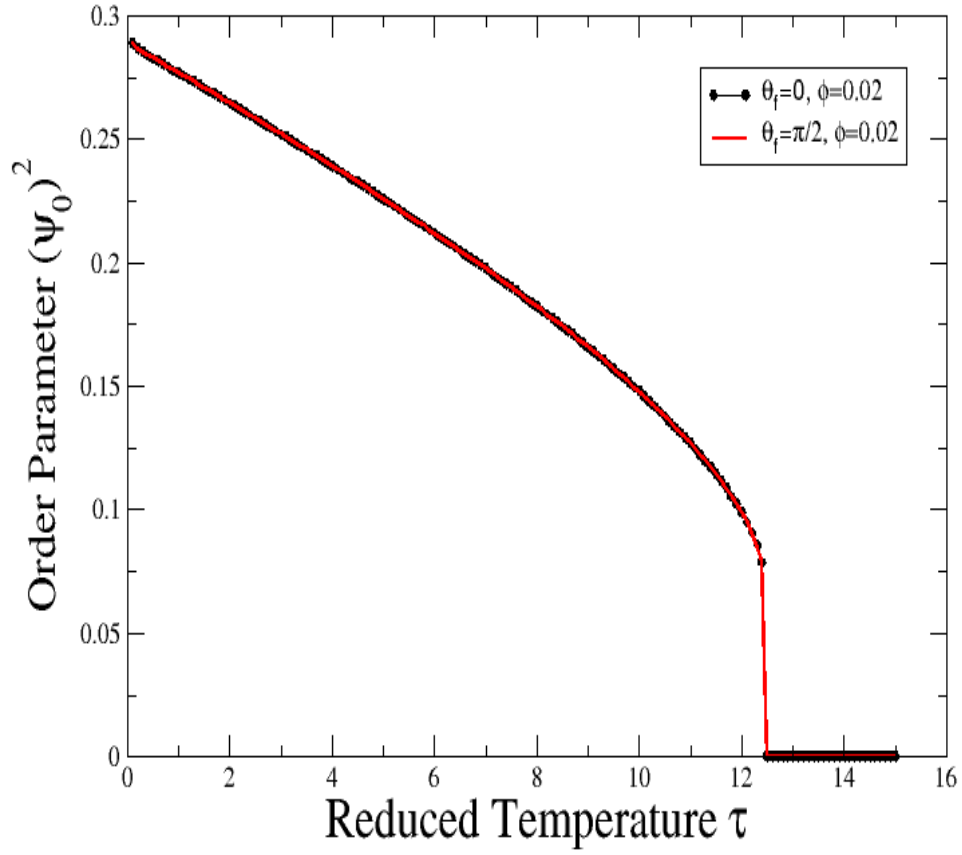


FIG. 5:  $\psi_0^2$  plotted against reduced temperature  $\tau = (T - T_2^*)/T_2^*$ ; plots show discontinuous jump for  $\phi = 0.02$ , independent of  $\theta_f$  values.

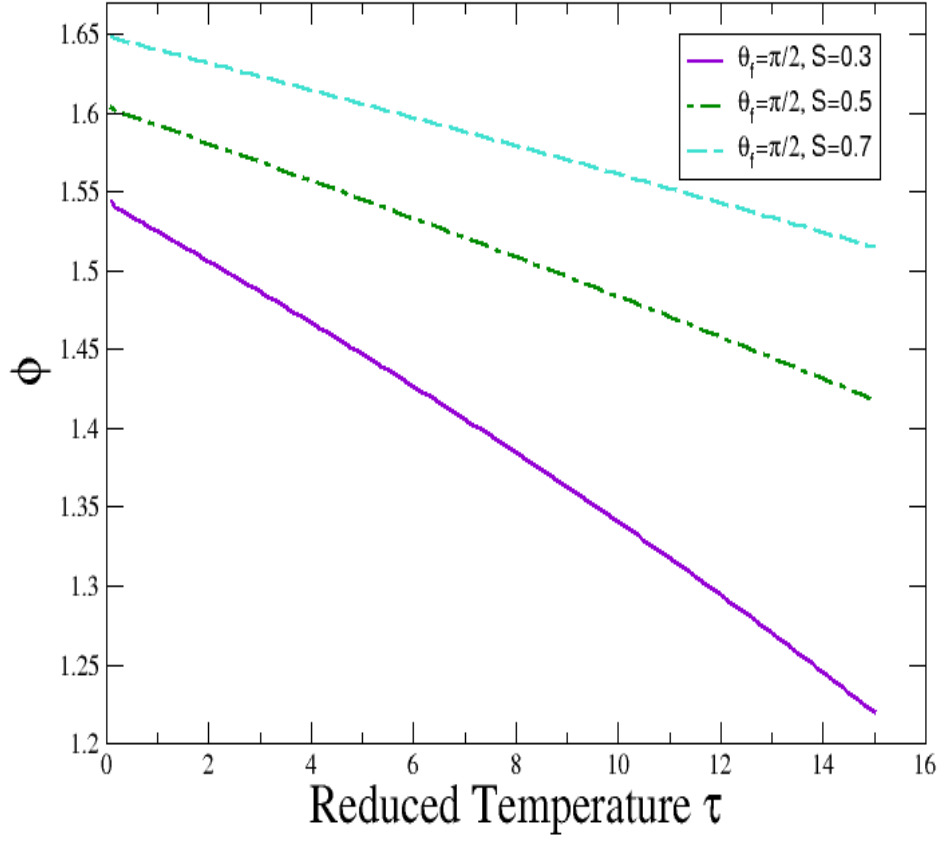


FIG. 6:  $\phi$  plotted against reduced temperature  $\tau = (T - T_2^*)/T_2^*$  shows a continuous decay over a wide range of values of  $S$  for  $\theta_f = \pi/2$ . The dot-dashed, dashed and solid lines respectively represent the cases for  $S = 0.3, 0.5$  and  $0.7$ .