Tricritical Phenomena and Cascades of Temperature Phase Transitions in a Ferromagnetic Liquid Crystal Suspension

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Abstract: We consider temperature-driven phase transitions occurring in a liquid crystal suspension of ferromagnetic particles within the Landau–de Gennes theory. The temperature dependences of the order parameters in the uniaxial model with a vector order parameter for the magnetic subsystem are obtained. The dimensionless expression for the free energy density of the suspension has been used for the study of the phase behavior general regularities of the system. Phase state diagrams of the suspension and temperature dependences of the order parameters of the liquid crystal and the ensemble of magnetic particles for different values of the phenomenological expansion coefficients are constructed. It is shown that the considered model admits the existence of a cascade of temperature phase transitions: isotropic phase–superparamagnetic nematic phase–ferromagnetic nematic phase. We have shown that in the mesomorphic state of the liquid crystal, the spontaneous magnetization can appear in a continuous way or by a jump with decreasing temperature, which corresponds to the tricritical behavior. The values of temperature and expansion coefficients corresponding to the tricritical and triple points are numerically found.

Keywords: Landau–de Gennes theory; ferromagnetic nematic; phase transition; triple point; tricritical point

1. Introduction

Since the appearance of the terms “ferronematics” and “ferrocholesterics” [1], introduced to denote hypothetical liquid crystal (LC) systems that possess a liquid ferromagnetic phase at room temperature, various types of LC-based magnetic nanoparticle suspensions have received considerable research attention [2–8]. Their relevance is primarily due to the fact that colloidal particles embedded in the LC matrix lead to the appearance of new and unusual properties of the nanocomposite. One of these unique features is the spontaneous ferromagnetic ordering of magnetic particles dispersed in the LC. The idea of obtaining a liquid ferromagnetic state, proposed in the pioneering work [1], is quite simple and natural. According to [1] ferromagnetic particles embedded in the LC must be strongly anisometric and their concentration must be sufficient to ensure the collective behavior of the system. Due to the presence of long-range order in the orientation of rod-shaped molecules, the LC matrix is able to order the anisometric impurity particles, acting for them as an effective external field. Despite the apparent simplicity of this representation, the experimental realization of a stable ferromagnetic nematic LC was announced relatively recently [9] for a dispersed phase of magnetic nanoplatelets.

In magnetic nematic LCs (for the simplest uniaxial case), the orientation order of the LC matrix can be described by the symmetric traceless tensor \( \eta_{ik} \), and the degree of ordering of the magnetic subsystem can be described by the magnetization \( \mathbf{M} \):

\[
\eta_{ik} = \sqrt{\frac{3}{2}} \eta (n_i n_k - \frac{1}{3} \delta_{ik}), \quad \mathbf{M} = M \mathbf{m}.
\]
Here, the scalar (nematic) order parameter $\eta$ characterizes the degree of ordering of the LC molecules relative to the major axis of the nematic order—the director $\mathbf{n}$. The value $M$ is a polar (magnetic) order parameter, which determines the degree of magnetization of the impurity subsystem in the direction of the unit vector $\mathbf{m}$. The normalization of the tensor $\eta_{ik}$ in (1) is chosen in such a way that the convolution of $\eta_{ik} \eta_{jk}$ gives $\eta^2$. Here and below the repeated tensor indices imply summation.

Brochard and de Gennes were the first to propose a theoretical description of ferromagnetic LC composites, using a rather simple continuum theory [1]. It was assumed that the suspension was in the mesophase and could be magnetized or compensated. The latter was the liquid crystal analogue of an antiferromagnet, i.e., in the absence of external fields it had equal volume fractions of impurity particles with oppositely oriented magnetic moments (see, e.g., [10]). Within the Brochard and de Gennes approach, the suspension is described by the LC director $\mathbf{n}$, the unit vector $\mathbf{m}$ characterizing the mean orientation of the magnetic moments of ferroparticles, and the local volume fraction of ferroparticles, which is responsible for the change in the magnetization magnitude. In the framework of the continuum theory, the description of the orientation structure of ferronematics is also possible by setting the fields of order parameter $\eta$ and $M$ (see, for example [11–14]), but in all the cases the control parameters are external fields, while temperature and concentration of particles are considered constant.

A theory to describe the appearance of spontaneous magnetization of a suspension induced by the temperature or impurity concentration changes was proposed before the experimental realization of stable ferromagnetic LC suspensions in [15,16]. In these studies, transitions between the ordinary isotropic magnetic fluid (I), the superparamagnetic nematic (SN) phase, and the ferromagnetic nematic (FN) phase were predicted within the Landau–de Gennes theory generalized to the LC-suspension case. In the isotropic phase, the nematic $\eta$ and magnetic $M$ order parameters remained zero. In both SN and FN phases, the LC is in an ordered state $\eta \neq 0$, and they differ in the fact that in the absence of external fields in the former phase the magnetization $M = 0$ and in the latter $M \neq 0$.

In the framework of the proposed model, the existence of a magnetic order without a nematic one is impossible, since the appearance of magnetization immediately leads to the ordering of the latter due to the orientation coupling between the particles and the matrix. Papers [15,16] demonstrate the possibility of a direct first-order phase transition from an isotropic phase to a ferromagnetic nematic phase (I–FN). It is also shown that the transition to a ferromagnetic nematic state can occur through the superparamagnetic nematic phase I–SN–FN, where magnetization occurs continuously, which corresponds to the phase transition of the second order.

Recently, a molecular-statistical theory of ferromagnetic LC suspensions [17] has been proposed where the same order parameters for LC and magnetic subsystems (1) as in [15] were used. In [17], the possibility of transitions between the phase states I, SN, and FN presented above is shown, and the expression for the free energy density obtained using the mean field method contains contributions found in the phenomenological approach [15]. Another statistical theory was proposed in [18], where, together with the magnetic order parameter $M$, an additional tensor parameter by analogy with LC was used to describe the orientational structure of the impurity particle ensemble. Inclusion of this order parameter allows one to consider the interaction of the particles with the LC, given its van der Waals origin. As is shown in [19] for spherical particles, this interaction is absent. Thus, anisometric particles in the LC matrix, instead of a superparamagnetic state with arbitrarily oriented magnetic moments, are in an antiferromagnetic state (compensated ferronemic). Molecular statistical theories of antiferromagnetic ferronematics are presented in [20–22].

As a starting point for a consistent construction of the phenomenological Landau–de Gennes theory of ferromagnetic LC suspensions, we will use the model proposed in [15] with some features corresponding to real ferronematics. Within the framework of the proposed theory, phase-state diagrams will be constructed in terms of temperature and coupling parameters of particles and the LC matrix, which has not been done before. We
have managed to show that in the ferromagnetic liquid crystal suspension the temperature phase transition cascade I–SN–FN includes both first- and second-order transitions, i.e., there is a tricritical behavior, for which the appropriate conditions have been obtained.

2. Theory

According to Landau’s theory [23], the suspension free energy density can be represented as an expansion on the invariants of the order parameters $\eta_{ik}$ and $M$. With an accuracy to the fourth order we obtain

$$F = \frac{A}{2} \eta^2_{ik} - \frac{B}{3} \eta_{ik} \eta_{kl} \eta_{li} + \frac{C}{4} (\eta_{ik}^2)^2 + \frac{\alpha}{2} M_i^2 + \frac{\beta}{4} (M_i^2)^2 +$$

$$+ \frac{\delta_1}{2} \eta_{ik} M_i M_k + \frac{\delta_2}{4} \eta_{ik}^2 M_i^2 + \frac{\delta_3}{4} \eta_{ik} \eta_{kl} M_i M_l + \ldots. \quad (2)$$

Here, the value $F$ is counted from the isotropic phase $F(\eta_{ik} = 0, M = 0)$, which corresponds to an ordinary ferrofluid. The free energy density $F$ is a function of temperature $T$, volume $V$ and order parameters $M$ and $\eta_{ik}$. The coefficients $A, B, C, \alpha, \beta, \delta_1, \delta_2,$ and $\delta_3$ are material parameters.

The nematic subsystem is very sensitive to temperature changes and at its decrease, it is able to order spontaneously due to features of the mesophase. The ferromagnetic subsystem does not have this property at the temperature of mesophase existence, and temperature changes do not induce the ferromagnetic order. Spontaneous magnetization of the impurity system in the absence of a field is induced only by the ordering of the LC matrix. Therefore, as is common for the Landau theory [23], we assume the coefficient $A = A_0 (T - T_*)$, where $T_*$ is the temperature of the absolute unstable isotropic phase relative to the transition to the nematic phase, and we assume the positive coefficient $A_0$ to be independent on temperature. The other phenomenological expansion coefficients for terms of higher order of smallness are also assumed to be constant.

Even at the stage of the free energy expansion we can draw some conclusions about the signs of a number of coefficients. Positive values of $C > 0, \beta > 0$ provide stability of the system with respect to the growth of nematic $\eta_{ik}$ and magnetic $M$ order parameters. The presence of the cubic invariant of the orientation tensor, i.e., $B > 0$, is associated with the physically nonequivalent states $\eta_{ik}$ and $-\eta_{ik}$, which correspond to the orientation anisotropy of the “easy-axis” and the “easy-plane” type, respectively.

Let us consider the phase states of the system when the magnetic and nematic ordering are spatially homogeneous. For the sake of certainty, let us also consider the case when the spontaneous magnetization arises in the direction of the main axis of the LC nematic order, i.e., the director $\mathbf{n} \equiv \mathbf{m}$ is the axis of easy-magnetization

$$\mathbf{M} = \mathbf{Mn}. \quad (3)$$

Using the Definitions (1) and (3), we calculate all the convolutions in the Expansion (2)

$$\eta_{ik}^2 = \eta^2, \quad \eta_{ik} \eta_{kl} \eta_{li} = \frac{1}{\sqrt{6}} \eta^3, \quad M_i^2 = M^2,$$

$$\eta_{ik} M_i M_k = \frac{2}{\sqrt{6}} \eta M^2, \quad \eta_{ik} \eta_{kl} M_i M_l = \frac{2}{3} \eta^2 M^2.$$

As a result, the free energy density (2) takes the form

$$F = \frac{A}{2} \eta^2 - \frac{B}{3 \sqrt{6}} \eta^3 + \frac{C}{4} \eta^4 + \frac{\alpha}{2} M^2 + \frac{\beta}{4} M^2 + \frac{\delta_1}{\sqrt{6}} \eta M^2 + \frac{1}{2} \left( \frac{\delta_2}{2} + \frac{\delta_3}{3} \right) \eta^2 M^2. \quad (4)$$
The equilibrium values $\eta$ and $M$ can be determined from the minimum free-energy density condition (4)

$$\frac{\partial F}{\partial \eta} = A\eta - \frac{\sqrt{6}}{6} B\eta^2 + C\eta^3 + \frac{\sqrt{6}}{6} \delta_1 M^2 + \left(\frac{\delta_2}{2} + \frac{\delta_3}{3}\right) \eta M^2 = 0,$$  \hspace{1cm} (5)

$$\frac{\partial F}{\partial M} = \alpha M + \beta M^3 + \frac{\sqrt{6}}{3} \delta_1 \eta M + \left(\frac{\delta_2}{2} + \frac{\delta_3}{3}\right) \eta^2 M = 0. \hspace{1cm} (6)$$

This system of equations has several solutions defining different phase states of the suspension. The first solution exists over the entire temperature range and corresponds to an isotropic phase with zero values of the order parameters ($\eta = 0, M = 0$). In fact, this state is an isotropic magnetic fluid, which is characterized by superparamagnetic behavior in an external magnetic field. The second solution

$$\eta = \eta_S = \frac{\sqrt{6} B}{12C} \left(1 \pm \sqrt{1 - \frac{24AC}{B^2}}\right), \hspace{1cm} M = 0 \hspace{1cm} (7)$$

corresponds to an ordered state with zero magnetization, i.e., superparamagnetic nematic. The dependence of $\eta_S$ on the temperature $T$ fully coincides with the similar equation of the orientation state of an impurity-free LC [24]. The plus sign in (7) corresponds to a nematic phase with the “easy-axis” type orientation anisotropy and the minus sign to the “easy-plane” one. Solutions (7) exist only when the expression under the root remains non-negative, i.e., at the temperature $T \geq T_t$, where

$$T_t = T_\ast + \frac{B^2}{24A_0C}. \hspace{1cm} (8)$$

To determine the temperature $T_{SI}$ of the first-order equilibrium phase transition between the SN and the I states, it is necessary to use the condition that the free energies of the corresponding phases are equal. The solution of equations $F = 0$ and (7) makes it possible to obtain, along with $T_{SI}$, the order parameter value $\eta_{SI}$ at the transition point

$$T_{SI} = T_\ast + \frac{B^2}{27A_0C}, \hspace{1cm} \eta_{SI} = \frac{2B}{3\sqrt{6}C}. \hspace{1cm} (9)$$

Thus, the isotropic liquid–superparamagnetic nematic transition is characterized by three temperatures—$T_\ast$, $T_t$, and $T_{SI}$. At high temperatures $T > T_t$, only phase I exists. As the temperature decreases at $T_{SI} < T < T_t$, this phase remains absolutely stable and the ordered SN phase is metastable. In the temperature range $T_\ast < T < T_{SI}$, the SN phase is absolutely stable and phase I is metastable. At low temperatures $T < T_\ast$, only the ordered phase is stable and the isotropic phase is completely unstable. Here, it should be noted that the ordered phase with orientational anisotropy of the “easy-plane” type ($\eta < 0$) is unstable or metastable in the whole temperature range and for the ordered SN phase an orientational anisotropy of the “easy-axis” type is understood everywhere.

Let us recall that in the considered model the solution $\eta = 0, M \neq 0$ does not exist. This is due to the fact that the ferromagnetic ordering plays the role of an external field for the nematic matrix. Due to the presence of orientation coupling between the LC molecules and ferroparticles, the ordering of the latter ($M \neq 0$) always induces the nematic order in the matrix $\eta \neq 0$.

The last solution, for which the LC order parameter $\eta = \eta_F$ and the magnetization $M$ are non-zero, corresponds to the ferromagnetic nematic. The analysis of this solution is a rather difficult task, which is due to some arbitrariness in the values of the unknown phenomenological expansion coefficients. For this reason, let us transform the expression (4) by introducing the notation
\[ \gamma = \delta_1, \quad \lambda = 3\delta_2 + 2\delta_3 \]  

(10)

and according to [25] we redefine the LC order parameter, the magnetization, and the temperature using the relations

\[ \eta = \frac{4B}{3\sqrt{6C}}\zeta, \quad M^2 = \frac{2k}{\beta} \mu^2, \quad t = 27 \frac{AC}{B^2}. \]  

(11)

In this case, the free energy density (4) can be rewritten in the dimensionless form

\[ f = \frac{3^6C^3}{2A^4} F = \frac{t}{4} \zeta^2 - \zeta^3 + \zeta^4 + a_1 (\mu^2 + \mu^4) + a_2 \zeta \mu^2 + a_3 \zeta^2 \mu^2, \]  

(12)

where

\[ a_1 = \frac{3^6 C^3 A^2}{24 B^4 \beta}, \quad a_2 = \frac{3^4 C^2 \gamma \alpha}{4 B^3 \beta}, \quad a_3 = \frac{9 C \lambda \alpha}{4 B^2 \beta}. \]  

(13)

According to the relations (11), the temperature \( T^* \) corresponds to the value \( t = 0 \). Minimization of the \( f \) (12) by the new variables \( \zeta \) and \( \mu \) allows us to obtain a system of equilibrium equations for the suspension

\[ \frac{\partial f}{\partial \zeta} = \frac{t}{2} \zeta - 3 \zeta^2 + 4 \zeta^3 + a_2 \mu^2 + 2 a_3 \zeta \mu^2 = 0, \]  

(14)

\[ \frac{\partial f}{\partial \mu} = \mu \left[ a_1 (2 + 4 \mu^2) + 2 a_2 \zeta + 2 a_3 \zeta^2 \right] = 0, \]  

(15)

which together with the thermodynamic stability conditions

\[ \frac{\partial^2 f}{\partial \zeta^2} = \frac{1}{2} - 6 \zeta + 12 \zeta^2 + 2 a_3 \mu^2 > 0, \]  

(16)

\[ \frac{\partial^2 f}{\partial \mu^2} = 2 a_1 (6 \mu^2 + 1) + 2 a_2 \zeta + 2 a_3 \zeta^2 > 0, \]  

(17)

\[ \frac{\partial^2 f}{\partial \zeta^2} \frac{\partial^2 f}{\partial \mu^2} - \left( \frac{\partial^2 f}{\partial \zeta \partial \mu} \right)^2 > 0 \]  

(18)

allows for the study of the phase state stability of the suspension in the case of uniaxial nematic matrix.

For the I phase \( \zeta = 0 \) and \( \mu = 0 \), the above conditions are greatly simplified and allow us to determine that \( a_1 > 0 \). In turn, the SN phase, for which \( \zeta \equiv \zeta_S \neq 0 \) and \( \mu = 0 \), is stable if the following conditions are met

\[ \frac{t}{2} - 6 \zeta_S + 12 \zeta_S^2 > 0, \]  

(19)

\[ a_1 + a_2 \zeta_S + a_3 \zeta_S^2 > 0. \]  

(20)

Real solutions of the equilibrium Equation (14) for the LC order parameter in the SN phase

\[ \zeta_S = \frac{3}{8} \left( 1 \pm \sqrt{1 - \frac{8}{9} t} \right) \]  

(21)

exist only if \( t \leq t_t \), where \( t_t = 9/8 \). The SN–I-state phase transition occurs at the temperature \( t_{SI} \), which can be determined from the condition of equality of free energy densities of the corresponding phases. Since we count the free energy density (12) from the isotropic phase, this condition finally takes a simple form

\[ \frac{t}{4} - \zeta_S + \zeta_S^2 = 0. \]  

(22)
The solution of this equation together with (21) gives the temperature of the equilibrium first-order phase transition SN–I and the value of the order parameter jump at the transition point

$$t_{SI} = 1, \quad \zeta_{SI} = 1/2. \quad (23)$$

These values can also be obtained by simple replacement of the old notations (9) with new ones using (11).

Let us proceed to the analysis of the solution for the FN phase for which $$\zeta \equiv \zeta_F \neq 0$$ and $$\mu \neq 0$$. From the definition of the parameters (13) and the free energy density (12), it follows that nontrivial solutions of the system of Equations (14) and (15) exist only at positive values of the parameter $$a_1$$. The expression in the square bracket of Equation (15) can be rewritten as

$$\mu^2 = -\frac{a_1 + a_2 \zeta_F + a_3 \zeta_F^2}{2a_1}, \quad (24)$$

from which we can conclude that for the occurrence of spontaneous magnetization ($$\mu^2 > 0$$), the inequality below must be fulfilled

$$a_1 + a_2 \zeta_F + a_3 \zeta_F^2 < 0,$$

resulting in the following relation

$$a_2^2 > 4a_1a_3.$$

Assuming the existence of ferromagnetic ordering of the dispersed phase ($$\mu \neq 0$$), $$\mu^2$$ can be excluded from Equation (14) using expression (24), and thus it is possible to obtain the relationship between the LC order parameter $$\zeta_F$$ in the FN phase and the temperature $$t$$

$$2b_1\zeta_F^3 - 3b_2\zeta_F^2 + b_3\zeta_F - a_1a_2 = 0, \quad (25)$$

where the following notations are used

$$b_1 = 4a_1 - a_3^2, \quad b_2 = a_2a_3 + 2a_1, \quad b_3 = ta_1 - 2a_1a_3 - a_2^2. \quad (26)$$

Let us rewrite the thermodynamic stability conditions (16)–(18) for the FN phase using the expression (24) in a more compact form

$$\frac{t}{2} - 6\zeta_F + 12\zeta_F^2 + 2a_3\mu^2 > 0, \quad (27)$$

$$a_3\zeta_F^2 + a_2\zeta_F + a_1 < 0, \quad (28)$$

$$6b_1\zeta_F^2 - 6b_2\zeta_F + b_3 > 0. \quad (29)$$

Transitions between the SN and the FN phases can occur as a first or second order phase transition. Let us begin with the second case, when spontaneous magnetization continuously appears in the FN as the temperature decreases. If we use the expression (24), the condition of equality of free energy densities of coexisting phases reads

$$\frac{a_1}{4} - \frac{a_2}{2}\zeta_{FS} - \left(\frac{a_2^2}{4a_1} + \frac{a_3}{2}\right)\zeta_{FS}^2 - \frac{a_2a_3}{2a_1}\zeta_{FS}^3 - \frac{a_2^3}{4a_1}\zeta_{FS}^4 = 0, \quad (30)$$

where $$\zeta_S = \zeta_F \equiv \zeta_{FS}$$ is the value of the LC order parameter at the transition point. The resulting equation together with (21) determine the temperature of the second-order phase transition between FN and SN phases

$$t_{FS} = -\frac{1}{a_3}\left[\frac{a_2}{a_3}(4a_2 + 3a_3 + 4\Delta) + 3\Delta - 8a_1\right], \quad (31)$$

where the following notation is introduced

$$\Delta = \sqrt{a_2^2 - 4a_1a_3}. \quad (32)$$
At the transition point itself, the magnetic particle order parameter is zero $\mu \equiv \mu_{FS} = 0$, and the LC order parameter $\zeta_{FS}$ can be determined by substituting the resulting temperature expression $t_{FS}$ in (21):

$$\zeta_{FS} = \frac{a_2 + \Delta}{2a_3}. \quad (33)$$

Expressions (31) and (33) do not allow for the consideration of the limit $a_3 = 0$. In this case, the solution of Equations (21) and (30) gives

$$t_{FS} = -\frac{2a_1(4a_1 + 3a_2)}{a_2}, \quad \zeta_{FS} = -\frac{a_1}{a_2}. \quad (34)$$

Note that expressions (31), (33), and (34) can also be obtained from the solution of Equations (21) and (25).

In the case when the FN–SN transition corresponds to the first-order phase transition, the order parameters at the transition point undergo a jump from the values of $\zeta = \zeta_S$ and $\mu = 0$ in the SN phase to $\zeta = \zeta_F$ and $\mu = \mu_F$ in the FN phase, respectively. To determine the temperature $t_{FS}$ of this transition, we again use the condition of equality of the free energies of the phases

$$t_{FS} = 4b_2^2 - \xi_F^4 + a_1 \left( b_F^4 + \mu_F^4 \right) + a_2 b_F^4 \mu_F^2 + a_3 b_F^2 \mu_F^2 = \frac{t_{FS} \xi_S^2}{4} - \xi_S^3 + \xi_S^4. \quad (35)$$

Equations (21), (24), (25) and (35) determine the temperature of the FN–SN first order phase transition and coefficients $a_1$, $a_2$, and $a_3$ in an implicit form.

Another possible situation is when the direct FN–I transition occurs, bypassing the SN phase. The condition of equality of free energies of coexisting phases for this case takes the form

$$t_{FI} = 4b_2^2 - \xi_{FI}^4 + a_1 \left( b_{FI}^4 + \mu_{FI}^4 \right) + a_2 b_{FI}^4 \mu_{FI}^2 + a_3 b_{FI}^2 \mu_{FI}^2 = 0. \quad (36)$$

Equation (36) together with Equations (24) and (25) determine the dependence of the FN–I transition temperature and jumps of the order parameters $\zeta_{FI}$ and $\mu_{FI}$ on the coefficients $a_1$, $a_2$, and $a_3$.

3. Phase Diagrams

As a generalization of the results described above, Figure 1 presents the phase state diagrams of the suspension in terms of the dimensionless temperature $t$ and the absolute value of the parameter $a_2$, which characterizes the intensity of the orientation interaction between the LC and the impurity subsystems. In Figure 1, the solid blue curve corresponds to the second order phase transition between ferromagnetic and superparamagnetic nematic states. The solid black curve defines the boundary between an isotropic magnetic fluid and a superparamagnetic nematic. In Figure 1 there is a triple point (T point) in which the I, SN, and FN states coexist. The temperature for this point coincides with the temperature $t_{SI} = t^T = 1$ of the SN–I transition. By solving the system of Equations (24), (25), and (36) under the condition $t = 1$, we obtain the value of $a_2 = a_2^T$ corresponding to the triple point for fixed $a_1$ and $a_3$. In Figure 1a this point corresponds to the parameter value $a_2^T = -1.241$, in Figure 1b–$a_2^T = -1.041$, and in Figure 1c–$a_2^T = -0.225$.

Figure 1a,b show that the coexistence curve of the SN and the FN phases contains a tricritical point (TC point), where the phase transition changes from the second to the first order or vice versa. To determine the tricritical temperature, we use Equation (25), which gives the LC order parameter in the FN phase and find $t$

$$t = \frac{1}{a_1 \zeta_F} \left[ -2b_1^2 \zeta_F^3 + 3b_2 \zeta_F^2 + \left( a_2^2 + 2a_1 a_3 \right) \zeta_F + a_1 a_2 \right]. \quad (37)$$
At the tricritical point, nematic order parameters of the FN and the SN states must coincide \( \xi_F = \xi_S \) and the first derivative of the temperature (37) with respect to the order parameter \( \xi_F \) must vanish
\[
\frac{dt}{d\xi_F} = 2 \left( -2a_3^2 + 8a_1 \right) \xi_F^2 + (-3a_2a_3 - 6a_1) \xi_F + a_1a_2 = 0, \quad (38)
\]
then the solution of this equation with Equation (33), for example, for fixed \( a_1 \) and \( a_3 \) allows us to find the tricritical value of the parameter \( a_2 = a_2^{TC} \). The temperature \( t^{TC} \), corresponding to TC point, can be obtained by substituting \( a_1, a_3 \) with the determined value \( a_2^{TC} \) into (31). In the particular case \( a_3 = 0 \), the relation between parameters \( a_1 \) and \( a_2 \) for the ‘TC point’ can be obtained in an analytical form
\[
a_1 = -\frac{a_2 \Lambda^{2/3} + \Lambda^{1/3} + 1}{\Lambda^{1/3}}, \quad \Lambda = 1 - 16a_2 + 4\sqrt{16a_2^2 - 2a_2}.
\quad (39)
\]
Thus, for \( a_1 = 0.65 \) and \( a_3 = 0 \) we get \( a_2^{TC} = -1.118, t^{TC} = 0.784 \); for \( a_1 = 0.65 \) and \( a_3 = -0.3 \) we obtain \( a_2^{TC} = -0.871 \) and \( t^{TC} = 0.662 \), respectively.

By comparing Figure 1a,b we see that for \( a_3 = 0 \) the transition from the SN phase or I phase to the FN phase occurs at higher values of parameter \( |a_2| \) in comparison to the case \( a_3 \neq 0 \). In addition, the TC point shifts to lower temperatures as the absolute value of \( a_3 \) increases.

Figure 1c shows a phase diagram in which the ‘TC point’ is absent and the SN–FN transitions are continuous, i.e., are the second-order transitions. Earlier, this result was obtained within the framework of the molecular-statistical theory [17]. The expression for the free energy density presented in [17], in addition to the contributions describing only the LC subsystem, contained terms proportional to \( \eta M^2 \) and \( \eta^2 M^4 \). These contributions do not depend on the temperature, including the volume fraction of the impurity and the mean-field constants, i.e., they have an energetic but not entropic origin. It should be noted that due to low concentration of the disperse phase, the expression for the internal energy of the suspension should not contain contributions proportional to \( M^2 \) and \( M^4 \), which are responsible for direct dipole–dipole interaction between magnetic particles. Thus, the presence of these contributions in the free energy density (4) has an entropic but not energetic origin, although in the model under consideration, it is assumed that the \( \alpha \) and \( \beta \) coefficients are independent of temperature.

\[\text{Figure 1. Phase diagrams in terms of temperature } t \text{ and absolute value of parameter } |a_2| \text{ for (a) } a_1 = 0.65, \ a_3 = 0 \text{ (b) } a_1 = 0.65, \ a_3 = -0.3 \text{ and (c) } a_1 = 0.15, \ a_3 = -0.15.\]
4. Temperature Dependences of Order Parameters

Figures 2–4 show temperature dependences of the nematic order parameter of the LC matrix $\zeta$, the magnetic particle order parameter $\mu$, and the dimensionless free energy density of the suspension $f$ for $a_1 = 0.65$, $a_3 = -0.3$ and different values of $a_2$. These dependencies correspond to the phase diagram (see Figure 1b), for which the tricritical point $a_{TC}^2 = -0.871$ and the triple point $a_T^3 = -1.041$. The solid curves show thermodynamically stable states and the dotted curves show unstable or metastable states. The FN phase corresponds to the blue curves ($\zeta \equiv \zeta_F, \mu \neq 0$) and the SN phase to the black curves ($\zeta \equiv \zeta_S, \mu = 0$); the horizontal line $\zeta = 0$ corresponds to the I phase and the vertical lines denote the first-order phase transitions between the different phase states of the suspension.

Figure 2. Temperature dependances of (a) the order parameter $\zeta$, (b) the order parameter $\mu$, (c) the free energy $f$ at $a_1 = 0.65, a_2 = -0.85, a_3 = -0.30$.

Figure 3. Temperature dependances of (a) the order parameter $\zeta$, (b) the order parameter $\mu$, (c) the free energy $f$ at $a_1 = 0.65, a_2 = -0.95, a_3 = -0.30$. 
Figure 4. Temperature dependances of (a) the order parameter $\zeta$, (b) the order parameter $\mu$, (c) the free energy $f$ at $a_1 = 0.65, a_2 = -1.05, a_3 = -0.30$.

Figure 2 corresponds to the case $|a_2| < |a_2^{TC}|$. In the absence of external magnetic fields at high temperatures, only an isotropic phase corresponding to an ordinary magnetic liquid is possible. As the temperature decreases, according to the phase diagram (Figure 1b) at $t_{SI} = 1$ there is a transition to the SN phase where there is no magnetic order $\mu$, and the LC order parameter $\zeta_S$, described by Equation (21), undergoes a jump from zero to $\zeta_{SI} = 1/2$ (see Figure 2a). With further decrease in temperature at $t = t_{FS} = 0.612$ and $\zeta_F = \zeta_S = \zeta_{FS} = 0.626$, the suspension begins to magnetize (see Figure 2b), i.e., the next continuous transition to the FN phase occurs. The occurrence of magnetic particle order induces additional orientational ordering of the LC medium, which is more evident in higher values of the matrix order parameter than in the case of a pure LC $\zeta_F > \zeta_S$. Figure 2c shows temperature dependences of the dimensionless free energy density $f$ of the suspension corresponding to all possible phase states: I, SN, and FN. The thermodynamically stable solutions shown in Figure 2a have been chosen based on the condition of minimum $f$.

Figure 3 corresponds to the condition $|a_2^{TC}| < |a_2| < |a_2^{T}|$. Like in the previous case (see Figure 2), at high temperatures the suspension is in the isotropic phase. It loses stability at $t = t_{SI}$ and there is a transition to the SN phase with a jump of LC order parameter (Figure 3a). This ordered phase remains stable until temperature $t = t_{FS} = 0.816$, at which a spontaneous jump in magnetization takes place (Figure 3b) and the transition to the ferromagnetic state occurs. The order parameters of the LC and the particles at the transition point undergo a jump from values $\zeta_S = \zeta_F = 0.572$ and $\mu = 0$ to $\zeta_F = \zeta_F = 0.656$ and $\mu = \tilde{\mu}_F = 0.280$, respectively. With a further decrease in temperature, the FN phase remains stable and there is an increase in the ordering of both the LC subsystem and the ensemble of particles. Stable solutions have also been determined from the free energy density minimum condition, which is shown in Figure 3c.

The behavior of the order parameters in the suspension at $|a_2^{T}| < |a_2|$ is shown in Figure 4. From the phase diagram in Figures 1b and 4, it can be seen that for $|a_2| = 1.05$ there is one direct transition from the I phase to the FN state, which occurs by jump at $t = t_{FI} = 1.009 > t_{SI}$. At the transition point, the LC and the particle order parameters undergo jumps from zero to $\zeta_{FI} = 0.715$ and $\mu_{FI} = 0.442$, respectively. The thermodynamically stable solutions in this case are also determined from the condition of the minimum free energy density $f$, shown in Figure 4c.

5. Conclusions

Within the framework of the phenomenological Landau–de Gennes theory we have studied the temperature-driven phase transitions in the suspension of ferromagnetic particles based on nematic LC. We have used the tensor and vector order parameters to describe
the orientation order of the LC and impurity magnetic subsystems. Depending on the temperature, the suspension can be in one of three phase states. One phase corresponds to the ordinary isotropic magnetic fluid (I) and the other two correspond to the superparamagnetic (SN) or the ferromagnetic (FN) nematic. During the analysis of the solutions to the system of equilibrium equations, we obtained the conditions for the phenomenological expansion coefficients that are necessary for the existence of the FN phase. We were the first to construct the phase state diagrams of the suspension in terms of temperature and the parameter of the orientation coupling between the LC and magnetic particles. Earlier it was found that depending on the phenomenological expansion coefficients in the suspension, the cascade of the I–SN–FN transitions or the I–FN transition is possible. We found that the transition between the SN and FN states exhibits tricritical behavior, i.e., it can be either the first or the second order transition. Earlier, in the framework of the phenomenological theory [16] and the molecular-statistical theory [17], the tricritical behavior was not found and the spontaneous magnetization can appear only in a continuous manner. We have constructed temperature dependences of the order parameters of the suspension and shown the possibility of transitions of both the first and the second orders. The advantage of the approach considered in this paper is that we use a dimensionless form of the free energy density of the suspension. This makes it possible to obtain equilibrium equations in a general form regardless of the specific form of the Landau expansion coefficients. In conclusion, we note that the considered theory is incomplete because it does not take into account the anisotropy of the particle shape. Elongated or disk-like particles require an additional inclusion of the tensor order parameter for the impurity subsystem into the description, as was done in the molecular statistical theory [18]. In the future, we plan to generalize the theory and take into account the nematic order parameter for the ensemble of impurity particles, which, in addition to the biaxial form of orientation tensors, will allow us to consider not only planar but also homeotropic coupling of LC molecules and particles.

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