PHYSICAL REVIEW E **101**, 030701(R) (2020)

Rapid Communications

Molecular-statistical theory of ferromagnetic liquid crystal suspensions

Danil A. Petrov
Physics of Phase Transitions Department, Perm State University, Bukirev St. 15, 614990 Perm, Russia

(Received 16 January 2020; accepted 3 March 2020; published 16 March 2020)

A tensor variant of molecular-statistical theory is developed, within the framework of which it is possible to describe the appearance of spontaneous magnetization of anisotropic ferromagnetic nanoparticles dispersed in a nematic liquid crystal. Along with the tensor order parameters characterizing the orientational ordering of the liquid crystal and dispersed anisometric particles, the vector order parameter determining the magnetization of the ensemble of particles is additionally taken into account. A comparison between the previously known phenomenological theories of ferronematics and the proposed molecular-statistical theory is made. Phase diagrams of the suspension are constructed and the mean-field theory parameters are calculated on the basis of experimental data available in the literature.

DOI: 10.1103/PhysRevE.101.030701

Fifty years ago Brochard and de Gennes presented their theoretical work in which they predicted unique magnetic fluids based on nematic liquid crystals, namely, ferronematics [1]. In the framework of the continuum theory they proposed, the orientation of liquid crystal molecules and magnetic particles were described using only one unit vector, namely, director $\hat{\boldsymbol{n}}$, i.e., the coupling of the liquid crystal molecules with the impurity particles was assumed to be absolutely rigid. After the synthesis of the first thermotropic ferronematics [2] it became clear that the model of strong coupling considered at [1] is not correct enough, because in real ferronematics the coupling energy is finite. That is why Burylov and Raikher in their series of papers [3–6] suggested the potential of a finite coupling between magnetic particles and the matrix

$$f_{\mathrm{BR}} = -\frac{W}{d} y_p (\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2. \tag{1}$$

Here W is the surface energy density of interaction between the particles and the liquid crystal matrix, which represents the anisotropic part of the surface tension energy, y_p is the volume fraction of the impurity, d is the transverse diameter of the rodlike particle (in the case of thin disks it is the disk thickness), and $\hat{\boldsymbol{m}}$ is a unit vector of particle magnetization. For rodlike particles the vector $\hat{\boldsymbol{m}}$ also defines the main axis of the nematic order of their long axes. If $W > 0$, the expression (1) is minimal at $\hat{\boldsymbol{n}} \parallel \hat{\boldsymbol{m}}$, which corresponds to the planar anchoring of the director and magnetization; if $W > 0$, the minimum (1) corresponds to the homeotropic anchoring of $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{m}}$ ($\hat{\boldsymbol{n}} \perp \hat{\boldsymbol{m}}$).

Another approach to describe the orientational coupling between the liquid crystal director $\hat{\boldsymbol{n}}$ and magnetization $\hat{\boldsymbol{m}}$ was introduced by Mertelj *et al.* [7]. They succeeded in synthesizing suspensions of hexaferrite disklike platelets in a nematic liquid crystal with spontaneous magnetization. In [8] it was suggested that ferromagnetic ordering of such particles is possible via their interaction with the liquid crystal matrix. Mertelj and Lisjak drew the analogy with the ferromagnetic solid crystal and assumed that in the obtained suspensions, magnetic moments of nanoparticles take the role of the spins, and the liquid crystal director $\hat{\boldsymbol{n}}$ corresponds to the direction of easy magnetization [9], thus, the role of orientation coupling between the particles and the director $\hat{\boldsymbol{n}}$ is performed by the magnetic crystallographic anisotropy. Due to the condition of uniaxial symmetry of the nematic phase, the contribution to the volume density of the coupling energy in the lowest order in powers $\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{m}}$ has the form [10]

$$f_{\mathrm{M}} = -\frac{1}{2}\kappa \mu_0 M_0^2 (\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2. \tag{2}$$

Here κ is a dimensionless coupling parameter, μ_0 is the magnetic permeability of the vacuum, and M_0 is the value of the suspension saturation magnetization without considering the diamagnetic contribution of the liquid crystal.

The expressions (1) and (2) are alike; both are proportional to $(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2$. In this Rapid Communication it will be shown that from a microscopic perspective these two approaches can be separated and each of them takes into account a different mechanism of orientation coupling of liquid crystal molecules and impurity particles. The contribution (1) is suitable for the description of the orientation coupling between a liquid crystal and both magnetic [11–15] and nonmagnetic particles [16,17]. The only condition is that the particles must have a shape anisotropy (e.g., rods or disks), because for spherical particles $W = 0$. The expression (2) was used when there is spontaneous magnetization of the disperse phase in the suspension [7,10,18]. However, even in the absence of an external magnetic field, the orientation order of both molecules and impurity particles can be preserved in the suspension, but the spontaneous magnetization is equal to zero. This state is sometimes called the superparamagnetic phase (or paramagnetic), but this is not quite correct. In the superparamagnetic state, the magnetic moments of the particles must be randomly oriented in space, which is only possible at temperatures higher than the clearing point of a nematic, when the suspension no longer differs from an ordinary magnetic fluid with isotropic dispersion medium. Below the clearing point in the absence of spontaneous magnetization due to the orientation coupling between the liquid crystal molecules and anisometric particles, the latter in the case of a planar anchoring are oriented parallel and antiparallel to the director of a liquid crystal with equal probability. Such suspensions were predicted in [1] and were called compensated ferronematics, which are liquid crystal analogs of antiferromagnetics (antiferromagnetic liquid crystal). Therefore, it is reasonable to call the ordered phase of the suspension with zero spontaneous magnetization the antiferromagnetic nematic phase, and that with nonzero magnetization the ferromagnetic nematic phase. Compensated suspensions within macroscopic theory using the Burylov and Raikher approach are considered in [19–21], including suspensions of ferroelectric particles in a liquid crystal [22,23], but with the rigid orientational coupling between subsystems. Thus, expression (2) is less universal than (1) and does not allow one to describe the compensated suspensions.

From a phenomenological perspective, expressions (1) and (2) are equivalent, as established in [24], but they only differently determine the coupling parameter of the liquid crystal director $\hat{\boldsymbol{n}}$ and magnetization $\hat{\boldsymbol{m}}$. Thus, the present work is devoted to combining the approaches of Burylov and Raikher and Mertelj *et al.* in the framework of molecular-statistical mean-field theory. This model makes it possible to describe the appearance of spontaneous magnetization of the suspension, to link the phenomenological parameters W and κ with the mean-field parameters and the order parameters of the suspension. As a result, the temperature dependence of the phenomenological parameters W and κ can be obtained.

Let us consider a homogeneous single-domain liquid crystal suspension as a binary mixture consisting of N_n molecules and N_p magnetic nanoparticles. The orientation of a separate rodlike molecule of a liquid crystal at a point $\boldsymbol{r}_\alpha$ will be described by a symmetric traceless tensor of the second rank

$$\nu_{ik}^{\alpha} = \sqrt{\frac{3}{2}}\left(\hat{\nu}_{\alpha i}\hat{\nu}_{\alpha k} - \frac{1}{3}\delta_{ik}\right), \tag{3}$$

where $\hat{\boldsymbol{\nu}}_\alpha$ is the unit vector along the main axis of the α molecule of the nematic ($\alpha = \overline{1, N_n}$). For an ensemble of impurity particles the similar value is constructed:

$$e_{ik}^{\beta} = \sqrt{\frac{3}{2}}\left(\hat{e}_{\beta i}\hat{e}_{\beta k} - \frac{1}{3}\delta_{ik}\right), \tag{4}$$

where $\hat{\boldsymbol{e}}_\beta$ is the unit vector along the main axis of the anisometric ferroparticle ($\beta = \overline{1, N_p}$). Henceforth the summation over repeated tensor indices is assumed.

An important feature of suspensions synthesized by Mertelj *et al.* [7] is that they used disklike platelets which have the homeotropic type of anchoring with liquid crystal molecules instead of the rodlike particles offered by Brochard and de Gennes. This fact allowed one to obtain a stable ferromagnetic ordering of the particles in the liquid crystal matrix. Unlike rodlike particles, the vector that defines the orientation of the platelet $\hat{\boldsymbol{e}}_\beta$ is a normal to its surface, which also coincides with the direction of the platelet magnetic moment [7]. As mentioned in [24], there exists a topological similarity between a thin disk with homeotropic anchoring and a thin rod with planar anchoring with the liquid crystal matrix. Thus, to avoid further confusion, by planar anchoring $\hat{\boldsymbol{\nu}}_\alpha \parallel \hat{\boldsymbol{e}}_\beta$ is meant.

To take into account the spontaneous magnetization of the suspension, it is necessary to introduce the vector order parameter, which is represented by the reduced magnetization

$$\boldsymbol{M} = \frac{1}{\mu N_p}\sum_{\beta=1}^{N_p}\boldsymbol{\mu}_\beta. \tag{5}$$

The vector $\boldsymbol{M}$ is associated with the magnetization of the suspension

$$\boldsymbol{\mathcal{M}} = \frac{\mu N_p}{V}\boldsymbol{M}. \tag{6}$$

Here $\boldsymbol{\mu}_\beta = \mu\hat{\boldsymbol{e}}_\beta$ are the magnetic moments of impurity particles and V is the suspension volume.

The macroscopic orientation tensors of suspension components and the vector order parameter can be obtained as a result of statistical averaging of the tensors (3),(4) and the vector $\hat{\boldsymbol{e}}_\beta$:

$$\eta_{ik} = \langle \nu_{ik}^{\alpha}\rangle, \quad S_{ik} = \langle e_{ik}^{\beta}\rangle, \quad \boldsymbol{M} = \langle \hat{\boldsymbol{e}}_\beta\rangle. \tag{7}$$

Let us represent the values (7) in terms of the unit vectors defining the main axes of the nematic order of liquid crystal molecules $\hat{\boldsymbol{n}}$ and the impurity particles $\hat{\boldsymbol{m}}$, for the latter $\hat{\boldsymbol{m}}$ is also the axis of the polar orientation order

$$\eta_{ik} = \sqrt{\frac{3}{2}}\eta\left(\hat{n}_i\hat{n}_k - \frac{1}{3}\delta_{ik}\right), \tag{8}$$

$$S_{ik} = \sqrt{\frac{3}{2}}S\left(\hat{m}_i\hat{m}_k - \frac{1}{3}\delta_{ik}\right), \tag{9}$$

$$\boldsymbol{M} = \langle \hat{\boldsymbol{e}}_\beta\rangle = M\hat{\boldsymbol{m}}. \tag{10}$$

Here the scalar nematic order parameter of the liquid crystal η and scalar nematic S and polar M particle order parameters are introduced

$$\eta = \langle P_2(\hat{\boldsymbol{n}}\hat{\boldsymbol{\nu}})\rangle, \quad S = \langle P_2(\hat{\boldsymbol{m}}\hat{\boldsymbol{e}})\rangle, \quad M = \langle P_1(\hat{\boldsymbol{m}}\hat{\boldsymbol{e}})\rangle, \tag{11}$$

where $P_1(x)$ and $P_2(x)$ are the first and the second Legendre polynomials, respectively.

In the mean-field approximation, the distribution function of the molecules and impurity particles ensemble is as follows:

$$w = (w_n)^{N_n}(w_p)^{N_p}, \tag{12}$$

where w_n and w_p are single-particle distribution functions of molecules and particles, respectively. Then according to [25,26] and the assumption of Mertelj *et al.* about the orientational coupling between a liquid crystal director and magnetization [7], the free energy of the suspension of hexaferrite platelets in a nematic liquid crystal in the absence of external fields can be presented as follows:

$$\begin{aligned} F\frac{v_n}{\lambda V} = {} & -\frac{1}{2}y_n^2\eta_{ik}\eta_{ik} + y_n\tau\langle \ln w_n\rangle + y_p\gamma\tau\langle \ln w_p\rangle \\ & - y_n y_p\gamma\omega\eta_{ik}S_{ik} - y_n y_p\gamma\omega_m\eta_{ik}M_iM_k. \end{aligned} \tag{13}$$

Here, $y_n = N_n v_n/V$ and $y_p = N_p v_p/V = 1 - y_n$ are the volume fractions of the suspension components (v_n and v_p are the volumes of a liquid crystal molecule and a particle, respectively) and $\gamma = v_n/v_p$. Here the role of the mean-field constant [27] is played by the value $\lambda = A_{nn}/v_n$, to which A_{nn}

is the intermolecular interaction energy. The mean-field parameters $\omega = A_{np}/A_{nn}$ and $\omega_m = A_m/A_{nn}$ describe the relative role of both nonmagnetic and magnetic orientation interaction between molecules and particles A_{np} and A_m, respectively, compared to the interaction only between molecules A_{nn}. Here $\tau = k_bT/\lambda$ (k_b is Boltzmann's constant) is the dimensionless temperature.

The first two terms in (13) take into account the free energy of the nematic matrix [27]. The third one is an entropic contribution of an ensemble of impurity particles [1]. The fourth term takes into account the orientation coupling between the molecules and particles and has a nonmagnetic van der Waals origin [26]. The last term describes the coupling between the nematic matrix and the magnetization of the dispersed phase and is analogous to the magnetic anisotropy energy in a solid ferromagnet [8]. In [28] it is experimentally established that even spherical magnetic particles cause an additional ordering of the liquid crystal matrix and significantly reduce the threshold of magnetic Fréedericksz transition in comparison with a pure liquid crystal and suspensions of nonmagnetic spherical particles. According to [28], this effect is explained by non-negligible local magnetic interactions between liquid crystal molecules and magnetic nanoparticles. Thus, in the free energy of liquid crystal suspension of anisometric magnetic particles there should be two independent contributions, which take into account the orientation coupling of the matrix and the particles of both nonmagnetic and magnetic origin. As noted in [29], for low-concentration suspensions in the absence of an external field, the only physical mechanism that aligns the nanoparticles is the interaction with the liquid crystal. Therefore, the expression (13) does not include contributions proportional to $S_{ik}S_{ik}$ and $S_{ik}M_iM_k$, which are responsible for direct interaction between particles. It should be noted here that for concentrated suspensions of platelike ferromagnetic particles based on the isotropic matrix [30,31] omitted contributions should be responsible for the appearance of ferromagnetic ordering, and in this case the effects of excluded volume should also be taken into account.

Let us consider the average energy of the suspension U, which can be determined from the expression (13):

$$U\frac{v_n}{\lambda V} = -\frac{1}{2}y_n^2\eta_{ik}\eta_{ik} - y_ny_p\gamma\omega\eta_{ik}S_{ik} - y_ny_p\gamma\omega_m\eta_{ik}M_iM_k. \tag{14}$$

Calculating the convolutions of the tensors (8),(9), and the vector (10)

$$\eta_{ik}\eta_{ik} = \eta^2, \quad \eta_{ik}S_{ik} = \frac{3}{2}\eta S(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2 - \frac{1}{2}\eta S,$$
$$\eta_{ik}M_iM_k = \frac{\sqrt{6}}{2}\eta M^2(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2 - \frac{\sqrt{6}}{6}\eta M^2, \tag{15}$$

it is easy to obtain the volume density of the energy (14) as follows:

$$\frac{U}{V} = -\frac{1}{2}\frac{\lambda}{v_n}y_n\bigg\{y_n\eta^2 - y_p\gamma\left(\omega\eta S + \frac{\sqrt{6}}{3}\omega_m\eta M^2\right) + y_p\gamma(3\omega\eta S + \sqrt{6}\omega_m\eta M^2)(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2\bigg\}. \tag{16}$$

From the expression (16) it is obvious that orientation coupling of the liquid crystal director $\hat{\boldsymbol{n}}$ and the magnetization $\hat{\boldsymbol{m}}$ is determined by two contributions [see the multiplier prior to $(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2$]. The first contribution does not depend on the degree of magnetization M and contains the ω parameter, whose origin is related to the anisotropy of the liquid crystal surface tension [5]. This parameter is the measure of anisometry of the particles which turns to zero if particles have the spherical shape. This contribution provides the orientation coupling of anisometric particles with the liquid crystal matrix, while the particles can also be nonmagnetic [32]. It should be noted that in the case of suspensions of ferroelectric particles in a liquid crystal [29,33], this parameter is related to the electric polarization of nematic molecules, which is induced by the electrical dipole moments of the particles. The second contribution which is proportional to $(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2$ into (16) depends on the degree of the liquid crystal order and the ferromagnetic order of the particles, namely, $\propto \eta M^2$. The parameter ω_m can be interpreted as a measure of the magnetic anisotropy energy. At $\omega = 0$ the expression (16) coincides with the one obtained earlier in [24], where the classical density functional theory for the liquid crystal suspension was used.

By comparing the expression (16) with (1) and (2), phenomenological parameters W and κ as functions of the suspension order parameters, i.e., temperature, can be determined:

$$W = \frac{3}{2}\frac{dy_n\lambda\omega\eta S}{v_p}, \quad \kappa = \sqrt{6}\frac{y_ny_p\lambda\omega_m\eta M^2}{v_p\mu_0M_0^2}. \tag{17}$$

At fixed external electric and magnetic fields, temperature, pressure, and homogeneous distribution of an impurity, order parameters of the suspension are constants, and therefore all the expression standing before $(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2$ in expression (16) can be considered as a phenomenological constant, which is defined from an experiment. Thus, it becomes clear from (16) that although the proposed approaches by Burylov and Raikher and Mertelj *et al.* proceed from different notions of the orientation coupling mechanisms between magnetic particles and liquid crystal molecules, they in fact introduce, respectively, either dimensional W, or dimensionless κ phenomenological parameters that take into account both nonmagnetic and magnetic coupling mechanisms. By combining the contributions (1) and (2), it is possible to write down the final expression for the volume energy density of orientational interaction (coupling) of anisometric ferromagnetic particles with the liquid crystal matrix in different ways:

$$f_{\mathrm{BR}} + f_{\mathrm{M}} = -\frac{\widetilde{W}}{d}y_p(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2 = -\frac{1}{2}\widetilde{\kappa}\mu_0M_0^2(\hat{\boldsymbol{n}}\hat{\boldsymbol{m}})^2, \tag{18}$$

where dimensional and dimensionless coupling parameters are redefined, respectively:

$$\widetilde{W} = W + \frac{d\kappa\mu_0M_0^2}{2y_p}, \quad \widetilde{\kappa} = \frac{2Wy_p}{d\mu_0M_0^2} + \kappa. \tag{19}$$

Thus, from the experiments [10,18] the value $\widetilde{\kappa}$ but not κ was determined.

After the substitution of expressions (17) into (19) it can be obtained

$$\widetilde{W} = \frac{d y_n \lambda}{2 v_p}(3\omega\eta S + \sqrt{6}\omega_m \eta M^2), \tag{20}$$

$$\widetilde{\kappa} = \frac{y_n y_p \lambda}{v_p \mu_0 M_0^2}(3\omega\eta S + \sqrt{6}\omega_m \eta M^2). \tag{21}$$

These expressions allow one to define the temperature dependencies of the phenomenological coupling parameters of liquid crystal and magnetization, respectively.

Now we come to equilibrium equations for the suspension order parameters η, S, and M. Given the fact that for a single-domain suspension in the absence of external electric and magnetic fields at positive values of the parameters ω and ω_m, the main axis of the nematic order of the liquid crystal $\hat{\boldsymbol{n}}$ coincides with the main axis of the nematic and the polar order of the particles $\hat{\boldsymbol{m}}$ (planar anchoring), then macroscopic tensors (8),(9) and the vector (10) can be characterized by a single vector $\hat{\boldsymbol{n}}$. As a result of the free energy (13) variation with respect to the molecule w_n and particle w_p orientation distribution functions taking into account the definitions (7) and (11), the equations of orientation equilibrium can be obtained:

$$\eta = \frac{3}{2}\frac{\partial \ln g(\sigma_n, 0)}{\partial \sigma_n} - \frac{1}{2}, \quad S = \frac{3}{2}\frac{\partial \ln g(\sigma_p, \zeta)}{\partial \sigma_p} - \frac{1}{2},$$

$$M = \frac{\partial \ln g(\sigma_p, \zeta)}{\partial \zeta}, \tag{22}$$

where the function g is determined:

$$g(\sigma, \zeta) \equiv \frac{1}{2}\int_{-1}^{1} \exp(\sigma x^2 + \zeta x) dx, \tag{23}$$

and dimensionless parameters are introduced:

$$\sigma_n = \frac{3}{2\tau}\left[y_n\eta + y_p\gamma\omega S + \frac{\sqrt{6}}{3}y_p\gamma\omega_m M^2\right],$$

$$\sigma_p = \frac{3}{2\tau}y_n\omega\eta, \quad \zeta = \frac{2\sqrt{6}}{3\tau}y_n\omega_m\eta M. \tag{24}$$

Equations (22) determine temperature dependencies of the order parameters η, S, and M.

Let us estimate material parameters according to [7,18] for the ferromagnetic suspension of hexaferrite platelets based on the liquid crystal 5CB; the average diameter of the platelet is $D = 70$ nm, the width is $d = 5$ nm, and the volume is $v_p = \pi d D^2/4 = 1.924 \times 10^{-23}$ m^3. The 5CB molecule volume can be estimated if it is known the liquid crystal molar mass $\mu_{\mathrm{LC}} = 0.249$ kg/mol and its mass density at the room temperature $\rho_{\mathrm{LC}} = 1020$ kg/m^3 [34], then $v_n = \mu_{\mathrm{LC}}/(\rho_{\mathrm{LC}} N_a) = 4.054 \times 10^{-28}$ m^3 ($N_a = 6.022 \times 10^{23}$ mol^{-1} is the Avagadro number) and $\gamma = v_n/v_p = 2.107 \times 10^{-5}$. To determine the mean-field constant for a pure liquid crystal, the formula $\lambda = k_B T_c/\tau_c = 1.934 \times 10^{-20}$ J should be used, where $T_c = 308.4$ K is the liquid crystal 5CB clearing point [35], and $\tau_c = 0.2202$ is a dimensionless temperature of the nematic-isotropic liquid transition [27]. As indicated in [18] the temperature of measurements is $T = 298.0$ K, which corresponds to a dimensionless temperature $\tau = T/\lambda = 0.2127$. According to [18] for the volume fraction of particles $y_p = 3 \times 10^{-4}$ the saturation magnetization of the suspension reaches $M_0 = \mu N_p/V = 50$ A/m, with the coupling parameter equal to $\widetilde{\kappa} = 110 \pm 70$.

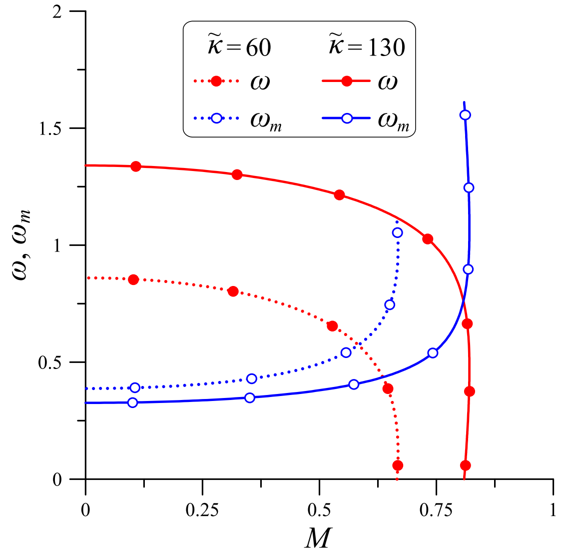

FIG. 1. Dependencies of the mean-field coupling parameters ω (red curves with filled circles) and ω_m (blue curves with open circles) on the polar order parameter M for $\widetilde{\kappa} = 60$ (dotted curves) and $\widetilde{\kappa} = 130$ (solid curves).

We can now proceed to determining the coupling parameters of the mean-field theory ω and ω_m for the estimations presented above. For this purpose, we have to solve the set of the equilibrium equations (22) with the additional equation (21). In [7] it is claimed that the obtained suspension was stable even after several months, but unfortunately the value of residual equilibrium magnetization is not given. Figure 1 presents the dependence of the coupling parameters ω and ω_m on the polar order parameter M, which determines the equilibrium value of the suspension magnetization in the absence of external fields $\mathcal{M} = M_0 M$. From Fig. 1 it is seen that for the fixed parameter $\widetilde{\kappa}$, the growth of the magnetization M corresponds to a decrease in ω (red curve with filled circles) and an increase in ω_m (blue curve with open circles). From Fig. 1 it can also be seen that the coupling parameter $\widetilde{\kappa} = 130$ (solid curve) corresponds to the higher magnetization M in comparison with $\widetilde{\kappa} = 60$ (dotted curve). It should be noted here that the possible maximum magnetization value does not correspond to $\omega = 0$, but accordingly for $\widetilde{\kappa} = 60$ there is a maximum of $M = 0.6681$ at $\omega = 0.1129$ and $\omega_m = 0.9855$, but for $\widetilde{\kappa} = 130$ there is a maximum of $M = 0.8207$ at $\omega = 0.4705$ and $\omega_m = 1.0727$. Thus, after experimentally determining the value of $\widetilde{\kappa}$ and the equilibrium value of spontaneous magnetization in the absence of an external magnetic field $\mathcal{M}$, the parameters ω and ω_m can be found, then using the set of equations (22) the temperature dependencies of the order parameters η, S, and M and the phenomenological coupling parameters $\widetilde{W}$ and $\widetilde{\kappa}$ can be obtained.

Figure 2 presents the diagrams of the suspension orientation phases in the plane of the reduced temperature T/T_c (T_c, the clearing point of the pure liquid crystal 5CB)—the coupling parameter ω_m. For any material parameters there is a

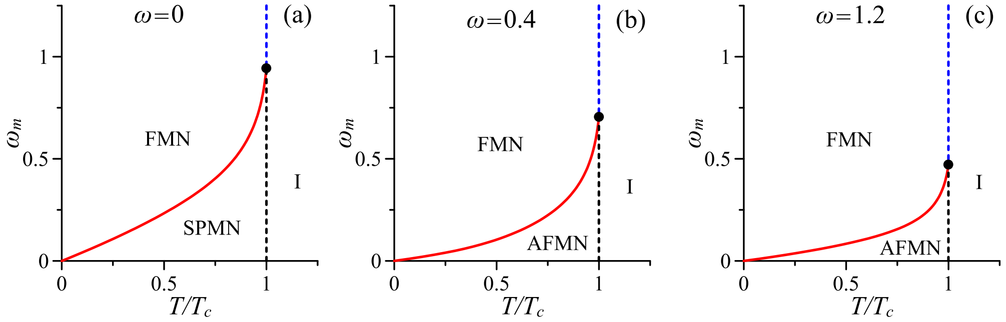

FIG. 2. Suspension phase diagrams in terms of reduced temperature and the mean-field coupling parameter ω_m for (a) $\omega = 0$, (b) $\omega = 0.4$, and (c) $\omega = 1.2$. Solid lines correspond to the second-order phase transitions, and dashed lines correspond to the first-order phase transitions.

high-temperature isotropic phase (I), where all the suspension order parameters, i.e., η, S, and M, are equal to zero. This phase is superparamagnetic like the ordinary isotropic ferrofluids. With a decrease in temperature depending on the values ω and ω_m there occurs a first-order phase transition (vertical dashed line) into ordered orientation phases with different magnetic properties. The first possible phase is a ferromagnetic nematic one (FMN), where $\eta > 0$, $S > 0$, and $M \neq 0$ (in the absence of an external magnetic field, the phases with $M > 0$ and $M < 0$ are equivalent). The second possible phase is an antiferromagnetic nematic (AFMN) phase, where $\eta > 0$, $S > 0$, and $M = 0$. This phase is characterized by equal fractions of the magnetic impurity with the oppositely oriented magnetic moments. The last orientation phase is possible only with $\omega = 0$ (spherical particles), i.e., a superparamagnetic nematic one (SPMN), where $\eta > 0$, $S = 0$, and $M = 0$. The relative difference in the temperatures of the transitions of ordered phase–isotropic liquid for a pure liquid crystal and for suspensions with the above-presented material parameters is less than 0.1% percent, so in Fig. 2 the vertical dashed line $T/T_c = 1$ corresponds to the boundary of isotropic phase existence. The filled black circles in Fig. 2 correspond to the triple I-FMN-SPMN point at $\omega_m = 0.9429$ for $\omega = 0$ [Fig. 2(a)] and I-FMN-AFMN triple points at $\omega_m = 0.7040$ for $\omega = 0.4$ and $\omega_m = 0.4703$ for $\omega = 1.2$ [see Figs. 2(b) and 2(c), respectively]. Figure 2 shows that with increasing ω, the I-FMN transition can take place at lower values of ω_m, and the FMN-AFMN transition occurs at higher temperatures.

In conclusion, a simple molecular-statistical theory of ferromagnetic liquid crystal suspensions of anisometric particles has been developed. The presented theory combines two previously known phenomenological approaches in which different expressions were offered to describe the volume energy density of orientational coupling of the liquid crystal director and the magnetization of impurity particles. The model predicts the existence of I-SPMN, I-AFMN, I-FMN, SPMN-FMN, and AFMN-FMN transitions induced by temperature changes. This theory can be extended in order to describe more complex systems, such as ferromagnetic chiral liquid crystal suspensions [36]. Using this theory, one can also describe orientational transitions in liquid crystal suspensions induced by electric and magnetic fields.

The author expresses his deep appreciation and gratitude to Professor Alexander N. Zakhlevnykh without whose ideas this work could not have appeared. This work was supported by the Russian Foundation for Basic Research, Project No. 19-02-00231.

---

[1] F. Brochard and P. G. de Gennes, J. Phys. (France) **31**, 691 (1970).
[2] S.-H. Chen and N. M. Amer, Phys. Rev. Lett. **51**, 2298 (1983).
[3] S. V. Burylov and Yu. L. Raikher, J. Magn. Magn. Mater. **85**, 74 (1990).
[4] S. V. Burylov and Yu. L. Raikher, Phys. Lett. A **149**, 279 (1990).
[5] S. V. Burylov and Yu. L. Raikher, Phys. Rev. E **50**, 358 (1994).
[6] S. V. Burylov and Yu. L. Raikher, Mol. Cryst. Liq. Cryst. **258**, 107 (1995).
[7] A. Mertelj, D. Lisjak, M. Drofenik, and M. Čopič, Nature (London) **504**, 237 (2013).
[8] A. Mertelj and D. Lisjak, Liq. Cryst. Rev. **5**, 1 (2017).
[9] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1984).
[10] N. Sebastián, N. Osterman, D. Lisjak, M. Čopič, and A. Mertelj, Soft Matter **14**, 7180 (2018).
[11] V. I. Zadorozhnii, V. Yu. Reshetnyak, A. V. Kleshchonok, T. J. Sluckin, and K. S. Thomas, Mol. Cryst. Liq. Cryst. **475**, 221 (2007).
[12] V. I. Zadorozhnii, T. J. Sluckin, V. Yu. Reshetnyak, and K. S. Thomas, SIAM J. Appl. Math. **68**, 1688 (2008).
[13] D. V. Makarov and A. N. Zakhlevnykh, Phys. Rev. E **81**, 051710 (2010).
[14] N. Podoliak, O. Buchnev, O. Buluy, G. D'Alessandro, M. Kaczmarek, Yu. Reznikov, and T. J. Sluckin, Soft Matter **7**, 4742 (2011).
[15] A. N. Zakhlevnykh and D. A. Petrov, J. Mol. Liq. **198**, 223 (2014).
[16] D. A. Petrov, P. K. Skokov, A. N. Zakhlevnykh, and D. V. Makarov, Beilstein J. Nanotechnol. **10**, 1464 (2019).
[17] C. Cirtoaje and E. Petrescu, Materials **12**, 4031 (2019).
[18] A. Mertelj, N. Osterman, D. Lisjak, and M. Čopič, Soft Matter **10**, 9065 (2014).

[19] A. N. Zakhlevnykh and D. A. Petrov, Phase Trans. **87**, 1 (2014).

[20] A. N. Zakhlevnykh and D. A. Petrov, Phys. Solid State **58**, 1906 (2016).

[21] A. N. Zakhlevnykh and D. A. Petrov, J. Magn. Magn. Mater. **401**, 188 (2016).

[22] V. Yu. Reshetnyak, S. M. Shelestiuk, and T. J. Sluckin, Mol. Cryst. Liq. Cryst. **454**, 201/[603] (2006).

[23] S. M. Shelestiuk, V. Yu. Reshetnyak, and T. J. Sluckin, Phys. Rev. E **83**, 041705 (2011).

[24] G. Zarubin, M. Bier, and S. Dietrich, J. Chem. Phys. **149**, 054505 (2018).

[25] A. N. Zakhlevnykh, M. S. Lubnin, and D. A. Petrov, J. Exp. Theor. Phys. **123**, 908 (2016).

[26] Yu. L. Raikher, V. I. Stepanov, and A. N. Zakhlevnykh, Soft Matter **9**, 177 (2013).

[27] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).

[28] A. Mouhli, H. Ayeb, T. Othman, J. Fresnais, V. Dupuis, I. R. Nemitz, J. S. Pendery, C. Rosenblatt, O. Sandre, and E. Lacaze, Phys. Rev. E **96**, 012706 (2017).

[29] L. M. Lopatina and J. V. Selinger, Phys. Rev. E **84**, 041703 (2011).

[30] M. Shuai, A. Klittnick, Y. Shen, G. P. Smith, M. R. Tuchband, C. Zhu, R. G. Petschek, A. Mertelj, D. Lisjak, M. Čopič, J. E. Maclennan, M. A. Glaser, and N. A. Clark, Nat. Commun. **7**, 10394 (2016).

[31] A. Mertelj, D. Lampret, D. Lisjak, J. Klepp, J. Kohlbrecher, and M. Čopič, Soft Matter **15**, 5412 (2019).

[32] D. A. Petrov and A. N. Zakhlevnykh, J. Mol. Liq. **287**, 110901 (2019).

[33] M. V. Gorkunov and M. A. Osipov, Soft Matter **7**, 4348 (2011).

[34] I. W. Stewart, *The Static and Dynamic Continuum Theory of Liquid Crystals: A Mathematical Introduction* (Taylor & Francis, London, 2004).

[35] H. Kneppe, F. Schneider, and N. K. Sharma, J. Chem. Phys. **77**, 3203 (1982).

[36] Q. Zhang, P. J. Ackerman, Q. Liu, and I. I. Smalyukh, Phys. Rev. Lett. **115**, 097802 (2015).