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On the theory of physical properties and phase transitions in ferrosmectics

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Abstract

Equilibrium thermodynamical characteristics of ferrosmectics are estimated under conditions when both magnetic and steric interparticle interactions are taken into account. Deformation and condensation phase transitions in ferrosmectics are studied.

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1. Introduction

Interest of investigators in compositions of magnetic colloidal particles suspended in liquid crystal systems has increased (see, for example, Refs. [1–5]) in recent years. This is explained by the fact that response of these compositions to external magnetic field is much more than those of pure liquid crystals. The possibility to control the inner structure of magneto-liquid crystal systems, and, therefore, their optical, rheological and other macroscopical properties using moderate or weak magnetic fields attracts the attention of researchers to these systems.

Smectic liquid crystals, contained one-domain ferromagnetic particles embedded inside their lyotropic layers, are called the ferrosmectics. These systems were synthesised by Fabre with collaborators and studied actively [4–9]. Very interesting peculiarities of structure and phase transitions in these systems have been discovered.

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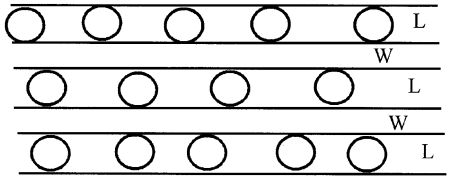

Fig. 1. Sketch of ferrosmectic structure. Circles – particles, L – lyotropic layers, W – water layers.

Theoretical models of ferrosmectics have not been developed practically. For example, in Ref. [5] the model of Lorenz–Weiss mean-field approximation is used to take into account effects of magnetodipole interparticle interaction. However, such mean-field models are too rough even for ordinary ferrocolloids on low-molecular base. For example, they predict a ferromagnetic phase transition, which is principally impossible in ferrocolloids. One can expect that the error of these models for lamellar systems, such as ferrosmectics, might be more than the error for ordinary ferrocolloids.

A phenomenological model of structural deformations in ferrosmectics was suggested in Ref. [10]. This model does not take into account the important peculiarities of magnetic interparticle interaction in these systems and does not allow to calculate macroscopical properties of samples (for example, components of tensor of magnetic susceptibility).

The attempt to obtain thermodynamical relations for ferrosmectics on the basis of regular methods of statistical physics was undertaken in Ref. [11]. Unfortunately, some errors were made in this work. Our aim now is to develop consistent statistical theory of equilibrium thermodynamical properties of ferrosmectics and to analyse phase transitions in these systems. At this point we will improve the errors of Ref. [11].

We suppose that the ferrosmectic has the same inner structure as samples in experiments [4,9]. Namely, lyotropic layers, containing ferroparticles, alternate with the layers of low-molecular liquid ("water") (Fig. 1). Ferroparticles are supposed to be identical spheres with a constant magnetic moment. Particles cannot move inside the lyotropic layers and leave them. The diameter of a particle $2a_p$ equals approximately the width of the lyotropic layers a_1 and the following inequality $2a_p < a_1 < 4a_p$ holds. For the sake of definiteness we assume smectic layers to be immovable on all boundaries of a sample. We neglect the interaction of molecules of both the lyotropic layers and "water" ones with the magnetic field. The magnetic field $\mathbf{H}$ is assumed to be small enough to use the linear law of magnetization.

2. The free energy of the system of ferroparticles in nondeformed sample

Let us introduce a cartesian coordinate system X, Y, Z with the axis OZ normal to layers of nondeformed ferrosmectic. Let the number of layers per unit of length in the OZ direction be $v = l^{-1}$ ($l = a_1 + a_0$, a_0 is the width of the "water" layer), n the number of the particles per unit square of lyotropic layer. Then $c = nv$ is the number

of the ferroparticles per unit volume of the sample. Let $\mathbf{H}_1$ be magnetic field inside the lyotropic layers, T be the absolute temperature in energetic units, $\alpha_1 = mH_1/T$ is the mean dimensionless field in the layers.

The volume density of free energy f_p of the particles system can be represented in the following form:

$$f_p = f_1 + f_d \,, \tag{1}$$

where f_1 is the free energy density of ideal gas of the particles in the field $\mathbf{H}_1$, f_d is the part of f_p, which occurs because of the magnetic interparticle interaction.

We estimate the energy f_1 using the well-known Langevine formulae

$$f_1 = -cT \ln \frac{sh\alpha_1}{\alpha_1} \approx -\frac{1}{6} Tc\alpha_1^2, \quad \alpha_1 \ll 1 \,. \tag{2}$$

The main problem of the theory is estimation of the magnitude f_d. In order to prevent any intuitive constructions, we use a regular method of thermodynamic perturbation theory [12,13].

According to the perturbation theory, f_d can be written as follows:

$$f_d = -TcnG \,, \tag{3}$$

$$G = \frac{1}{2} \left(\frac{4\pi\alpha_1}{sh\alpha_1} \right)^2 \int \varphi(Z) \exp(\alpha_1(\mathbf{e}_1 + \mathbf{e}_2)) \left[\exp\left(-\frac{U_d(\mathbf{e}_1, \mathbf{e}_2, \mathbf{r})}{T} \right) - 1 \right] \mathrm{d}\mathbf{e}_1 \, \mathrm{d}\mathbf{e}_2 \, \mathrm{d}\mathbf{r} \,,$$

$$\mathbf{e}_{1,2} = \frac{\mathbf{m}_{1,2}}{m} \,.$$

Here $\mathbf{m}_1$ and $\mathbf{m}_2$ are the magnetic moments of two interacting particles, U_d is the potential of their magnetodipole interaction, $\mathbf{r}$ is the radius-vector, connecting the centres of these particles, $\varphi(Z)$ is the one-particle distribution function along the axis OZ. Integration in Eq. (3) is made so that the particles do not overlap.

Taking into account that the particles are in the lyotropic layers, one can write

$$\varphi(Z) \approx \delta(Z - lp), \quad p = 0, \pm 1, \pm 2, \ldots \,, \tag{4}$$

where $\delta(x)$ is the delta function.

The perturbation theory approximation is suitable, if $\max|U_d/T|$ is not more than unity. In this situation one can expand the exponent of Eq. (3) as a power series in U_d/T and write

$$\exp\left(-\frac{U_d}{T} \right) \approx 1 - \frac{U_d}{T} + \frac{1}{2} \left(\frac{U_d}{T} \right)^2 \,. \tag{5}$$

Substituting Eq. (5) into Eq. (3) and, taking into account the strong inequality $\alpha_1 \ll 1$, after simple calculations one obtains

$$G \approx [g_0 + g_{1X}(\alpha_{1X}^2 + \alpha_{1Y}^2) + g_{1Z}\alpha_{1Z}^2] \,, \tag{6}$$

$$g_0 = q_0 + p_0, \quad g_{1J} = q_{1J} + p_{1J}, \quad J = X, Y, Z \,,$$

$$q_0 = \frac{1}{4(4\pi)^2} \int \left(\frac{U_d(\mathbf{e}_1, \mathbf{e}_2, \mathbf{r}_0)}{T} \right)^2 \mathrm{d}\mathbf{e}_1 \, \mathrm{d}\mathbf{e}_2 \, \mathrm{d}X \, \mathrm{d}Y \,,$$

$$p_0 = \frac{1}{2(4\pi)^2} \sum_{p=1}^{\infty} \int \left(\frac{U_d(\mathbf{e}_1, \mathbf{e}_2, \mathbf{r}_p)}{T} \right)^2 \mathrm{d}\mathbf{e}_1 \, \mathrm{d}\mathbf{e}_2 \, \mathrm{d}X \, \mathrm{d}Y \,,$$

$$q_{1J} = \frac{1}{(4\pi)^2} \int \mathbf{e}_{1J}^2 \left(-\frac{U_d(\mathbf{e}_1, \mathbf{e}_2, \mathbf{r}_0)}{T} \right) \mathrm{d}\mathbf{e}_1 \mathrm{d}\mathbf{e}_2 \, \mathrm{d}X \, \mathrm{d}Y \,,$$

$$p_{1J} = \frac{1}{(4\pi)^2} \sum_{p=1}^{\infty} \int \mathbf{e}_{1J}^2 \left(-\frac{U_d(\mathbf{e}_1, \mathbf{e}_2, \mathbf{r}_p)}{T} \right) \mathrm{d}\mathbf{e}_1 \, \mathrm{d}\mathbf{e}_2 \, \mathrm{d}X \, \mathrm{d}Y \,,$$

$$\mathbf{r}_0 = (X, Y, 0), \quad \mathbf{r}_p = (X, Y, pl) \,.$$

At the derivation of Eq. (6) we neglected the small terms proportional to $\alpha_1^2 (U_d/T)^2$ and less.

Integral in relation (3) has a peculiarity. The fact is that due to the potential U_d depending on interparticle distance as r^{-3}, the result of integration depends on the shape of integration [14].

The field $\mathbf{H}_1$ must be equal to macroscopical field in the region where the interacting particles are placed. For this reason we choose the integration volume as an infinitive cylinder with the axis directed along $\mathbf{H}_1$, passing across the centre of one particle. The length of this cylinder is much larger than its diameter. It means that, calculating p_{1Z} in Eq. (6) we need, first, to perform a summation over p and then to integrate with respect to X and Y. Calculating p_{1X} we need, first, to integrate over X, Y and then to sum over p. We must calculate p_0 and q_0 in such a way that $|\mathbf{r}_0| > 2a_p$.

The results of such calculations when $a_1 \approx 2a_p$ are

$$g_0 = \frac{\pi}{12} \gamma^2 (2a_p)^2 \left(1 + \frac{\pi^4}{45} \frac{a_1^4}{l^4} \right), \quad g_{1X} = \frac{1}{3} v\nu\gamma \frac{l}{a_1}, \quad g_{1Z} = \frac{2}{3} v\nu\gamma \left(2 - \frac{l}{a_1} \right) \,,$$

$$v = \frac{4\pi}{3} a^3, \quad \gamma = \frac{m^2}{(2a_p)^3 T} \,. \tag{7}$$

Here γ is the dimensionless parameter of magnetodipole interaction between the particles.

Substituting Eq. (7) into Eq. (6), then its result into (1) and then in the first relation of Eq. (3), using Eq. (2), we get

$$f_p = -\nu T \left[\frac{1}{6} \alpha_1^2 + \rho\gamma \left(\frac{l}{3a_1} (\alpha_{1X}^2 + \alpha_{1Y}^2) + \frac{2}{3} \left(2 - \frac{l}{a_1} \right) \alpha_{1Z}^2 + n g_0 \right) \right] \,. \tag{8}$$

Here $\rho = v\nu v$ is the volume concentration of the particles.

The components of the sample magnetization $\mathbf{M}$ are

$$M_X = -\frac{\partial f_p}{\partial H_{1X}} = \chi_{||} H_{1X}, \quad M_Z = -\frac{\partial f_p}{\partial H_{1Z}} = \chi_\perp H_{1Z} ,$$

$$\chi_{||} = \chi_L \left(1 + \pi \frac{l}{a_1} \chi_L\right), \quad \chi_\perp = \chi_L \left(1 + 2\pi\chi_L \left(2 - \frac{l}{a_1}\right)\right) ,$$

$$\chi_L = \frac{2}{\pi}\rho\gamma , \tag{9}$$

where χ_L is the Langevin initial susceptibility of dilute ferrocolloid.

Relations (9) allow us to make the following conclusions. First, magnetodipole interaction between the particles increases the initial susceptibility $\chi_{||}$ corresponding to orientation of the field $\mathbf{H}_1$ along the smectic layers. When this field is perpendicular to these layers, the interparticle interaction leads to increase of the corresponding susceptibility $\chi_\perp$ when $l < 2a_1$ and to its decrease when $l > 2a_1$. Second, the susceptibility $\chi_{||}$ is more than $\chi_\perp$ if the inequality $l > 4a_1/3$ holds; $\chi_{||} < \chi_\perp$ in the opposite case.

3. The structure deformations in the ferrosmectics

It is well known (see, for example, Refs. [15,16]) that periodical deformations (the Helfrich deformations) of smectic structure occur when the sample is placed in sufficiently large magnetic field normal to the smectic layers. In ferrosmectics these structure phase transitions occur in the fields by several orders of value smaller than those for pure smectics [5]. The aim of this part of the work is the analysis of critical parameters of the Helfrich phase transitions in ferrosmectics.

Let $\mathbf{u}(X,Z) = (0,0,u)$ be a small two-dimensional displacement of the layers inside the ferrosmectic. Under the presence of a weak external field $\mathbf{H}_e$ the magnetic free energy of the sample is

$$F_m = \int f_m \, \mathrm{d}V ,$$

$$f_m = -\tfrac{1}{2}(\mathbf{H}_e \mathbf{M}) . \tag{10}$$

The expression in Eq. (10) is to be integrated over all the volume of the sample. We assume that the field $\mathbf{H}_e$ is directed along the axis OZ, i.e., it is normal to the sample layers.

Let $\mathbf{H}_1$ and $\mathbf{H}_1^o$ be fields inside of deformed and nondeformed lyotropic layer, respectively, $\mathbf{h}_1 = \mathbf{H}_1 - \mathbf{H}_1^o$ ($h_1 \ll H_1^o$), ξ is a unit vector normal to the surface of the deformed layer (Fig. 2).

We denote by $\kappa_{||}$ and $\kappa_\perp$ the susceptibilities of one layer corresponding to orientations of the local magnetic field parallel and perpendicular to the layer surface. It is obvious that $\kappa_i = \chi_i/(a_1 v)$, where $i = ||, \perp$.

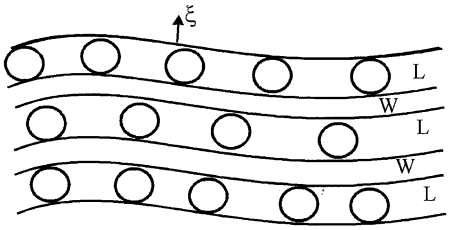

Fig. 2. Sketch of deformated ferrosmectic. Notations are the same as in Fig. 1.

Let $H_{1||}$ and $H_{1\perp}$ be components of the local magnetic field inside the lyotropic layer, parallel and perpendicular to its deformed surface, $M_{||}$ and $M_{\perp}$ the corresponding components of the local magnetization. It is clear that $M_J = \chi_J H_{1J}$ where $J = ||, \perp$. Substituting this relation into Eq. (10) and taking into account that $H_1^o = H_e/\mu_1$ ($\mu_1 = 1 + 4\pi\kappa_\perp$), after simple transformations we obtain

$$f_m = -\frac{H_e^2}{2}\left[\frac{1}{\mu_1}\chi_\perp + \chi_\perp \varepsilon_Z + \chi_a\left(\xi_X^2\left(\frac{1}{\mu_1} + \varepsilon_Z\right) - \xi_X\xi_Z\varepsilon_X\right)\right],$$

$$\chi_a = \chi_{||} - \chi_\perp, \quad \varepsilon = \frac{\mathbf{h}_1}{H_1^o}. \tag{11}$$

Let us consider the following small deformations:

$$u = u_0(Z)\cos kX \tag{12}$$

For small deformations, the following strong inequalities hold:

$$u_0 \ll a_1, a_0; \quad ka_1, ka_0 \ll 1.$$

In the linear approximation in u

$$\xi_X = \frac{\partial u}{\partial X}, \quad \xi_Z = 1. \tag{13}$$

It will be shown below that in this approximation $\varepsilon_{X,Z} \sim \xi_X$. Taking into account the character of dependence of ξ_X on coordinate X, one can show that the result of integration in Eq. (10) of the terms noneven over ξ_X is zero. Therefore, without loss of accuracy, one can rewrite Eq. (11) in the following form:

$$f_m = \frac{H_e^2}{2}\left[\frac{1}{\mu_1(v)}\chi_\perp(v) + \chi_a\left(\frac{1}{\mu_1(v)}\xi_X^2 - \xi_X\varepsilon_X\right)\right]. \tag{14}$$

In order to calculate ε_X we introduce a local cartesian coordinate system with the origin in the middle of nondeformed lyotropic layer, and axes x, y, z aligned along X, Y, Z, respectively. Supposing that the characteristic scale of changing of $u_0(Z)$ is much more than a_0, a_1, we write on the scales of l:

$$u(x) = u_0 \cos kx, \quad u_0 = const. \tag{15}$$

Let $\mathbf{H}_0$ and $\mathbf{H}_0^o$ be the local fields inside the deformed and nondeformed "water" layer, $\mathbf{h}_0 = \mathbf{H}_0 - \mathbf{H}_0^o$. It is convenient to introduce the magnetic potentials ψ_1, ψ_0 by the rule

$$\mathbf{h}_1 = grad\,\psi_1, \quad \mathbf{h}_0 = grad\,\psi_0\,. \tag{16}$$

Because the electric flux is absent, the Laplas equations $\Delta\psi_1 = \Delta\psi_0 = 0$ are fulfilled. The conditions of magnetostatics and periodicity of the sample give

$$\mu_0(\xi\mathbf{H}_0) = \mu_1(\xi\mathbf{H}_1), \quad [\xi \times \mathbf{H}_0] = [\xi \times \mathbf{H}_1], \quad z = \tfrac{1}{2}a_1 + u\,,$$

$$\mu_0(\xi\mathbf{H}_0)|_{z=a_0+a_1/2+u} = \mu_1(\xi\mathbf{H}_1)|_{z=-a_1/2+u}\,,$$

$$[\xi \times \mathbf{H}_0]|_{z=a_0+a_1/2+u} = [\xi \times \mathbf{H}_1]|_{z=-a_1/2+u}\,, \tag{17}$$

where

$$\xi_X \approx \frac{\partial u}{\partial X}, \quad \xi_Y \approx \frac{\partial u}{\partial Y}, \quad \xi_Z \approx 1$$

and $\mu_0 \approx 1$ is the magnetic penetration of the "water" layer.

We seek the potentials ψ_i in the following form:

$$\psi_i = [A_i \exp(kz) + B_i \exp(-kz)]\cos kx\,,$$

$$A_i, B_i = const., \quad i = 0, 1\,. \tag{18}$$

Substituting expressions (18) into boundary conditions of Eq. (17), taking into account the conditions $ka_{0,1} \ll 1$ and $\mu_0 \approx 1$ after simple however combersome calculations, one can obtain

$$A_i \approx B_i \approx -u_0 H_e W\,,$$

$$W \approx \frac{2\pi\kappa_\perp a_0}{\mu_1(\mu_1 + a_0)}\,. \tag{19}$$

Substituting Eq. (19) into Eq. (18) and, further, into Eq. (14), averaging result over lyotropic layer and taking into account that $ka_1 \ll 1$, we find the average density of free energy

$$\langle f_m \rangle = -\frac{H_e^2}{2}\left[\frac{\chi_\perp(v)}{\mu_1(v)} + \chi_a Q\left(\frac{\partial u}{\partial X}\right)^2\right]\,,$$

$$Q = \frac{1}{\mu_1} + W\,. \tag{20}$$

It follows from general theory of small deformations that the local density v of lyotropic layers depends on $u_0(Z)$ as follows:

$$v(Z) \approx v_0\left(1 - \frac{\mathrm{d}u_0}{\mathrm{d}Z}\right)\,, \tag{21}$$

where v_0 is the value of v for a nondeformed sample.

Let us denote

$$\delta v = v(Z) - v_0 = -v_0 \frac{\mathrm{d}u_0}{\mathrm{d}Z}, \quad \Phi(Z) = \frac{\chi_\perp(v)}{\mu_1(v)} .$$

In the quadratic approximation in δv

$$\Phi(v) \approx \Phi(v_0) + \Phi'\delta v + \tfrac{1}{2}\Phi''(\delta v)^2 . \tag{22}$$

Simple calculations give

$$\Phi'' = 2a_1 \frac{\kappa_0}{\mu_{01}} \varphi \left(1 - \frac{\kappa_0}{\mu_{01}}\right) ,$$

where

$$\kappa_0 = \frac{m^2 n}{3a_1 T}, \quad \varphi = 4n\gamma \left(2 - \frac{l}{a_1}\right) ,$$

$$\mu_{01} = 1 + 4\pi\kappa_0 .$$

Here κ_0 and μ_{01} are values of $\kappa_\perp$ and μ_1 for a nondeformed sample.

Taking into account Eq. (22), relation (20) can be written as

$$\langle f_m \rangle = \langle f_{m0} \rangle - \frac{H_e^2}{2} \left[\frac{1}{2} v_0^2 \left(\frac{\mathrm{d}u_0}{\mathrm{d}Z}\right)^2 + \chi_a Q \left(\frac{\partial u}{\partial X}\right)^2\right) , \tag{23}$$

where f_{m0} means the value of f_m for a nondeformed ferrosmectic.

In the absence of a magnetic field the free energy of deformed sample is the sum of the elastic free energy δF_e and the free energy δF_d arising due to change of energy of the particle dipole–dipole interaction. Using standard relations to δF_e and taking into account Eqs. (8) and (12), we have

$$\delta F_e = \frac{1}{2} \int \left[K_1 \left(\frac{\partial^2 u}{\partial X^2}\right)^2 + K_2 \left(\frac{\partial^2 u}{\partial Z^2}\right)^2 + C \left(\frac{\partial u}{\partial Z}\right)^2\right] \mathrm{d}\mathbf{R} ,$$

$$\delta F_d = -\beta \int \left(\frac{\partial u}{\partial Z}\right)^2 \mathrm{d}\mathbf{R} ,$$

$$\beta = 40 T n^2 p_0 v_0 . \tag{24}$$

We place the origin of coordinate system (X, Y, Z) in the middle of our sample. Let $2L$ be its thickness. We suppose that the sample is placed between two parallel rigid plates and deformations on the sample boundaries are equal to zero ($u_0(z = \pm L) = 0$). As usual, assuming that $u_0(Z) = U \cos qZ$ ($q = \pi/2L$) and substituting this expression into Eqs. (23), (24) and (10), one obtains for free energy δF of the sample in external magnetic field:

$$\begin{aligned} \delta F &= \delta F_m + \delta F_e + \delta F_d \\ &= \tfrac{1}{2} V \langle \cos^2 kX \cos^2 qZ \rangle U^2 [K_1 k^4 + K_2 q^4 + Bq^2 - H_e^2 \Phi'' \tfrac{1}{2} v_0 q^2 - H_e^2 \chi_a Q k^2] , \\ B &= C - \beta . \end{aligned} \tag{25}$$

Let us consider now several characteristic situations.

(1) $\chi_a > 0$, $B > 0$: In this case the ordinary Helfrich deformations can appear in the ferrosmectic. Indeed, the free energy δF is negative when the following inequality holds:

$$H_e > H_{ec}, \quad H_{ec}^2 = \frac{K_1 k^4 + K_2 q^4 + Bq^2}{\chi_a Q k^2 + \Phi'' v_0 q^2/2} \,. \tag{26}$$

The second-order deformational phase transition takes place in this situation. The critical wave number k_c in the point of the phase transition corresponds to a minimum of H_{ec} as function of k. Taking into account, that as a rule $\chi_a Q k^2 \gg \Phi'' v_0 q^2$, we obtain

$$k_c^2 \approx \sqrt{\frac{K_2 q^4 + Bq^2}{K_1}}, \quad H_{ec}^2 \approx \frac{2}{\chi_a Q} K_1 k_c^2 \,. \tag{27}$$

Because for ferrosmectics the parameter χ_a is much more than that for pure liquid crystals, H_{ec} for ferrosmectic is much smaller than that for pure smectics.

(2) $B > 0$, $\chi_a < 0$: The longitudinal deformations with $k = 0$ and $q = \pi/2L$ can occur now in ferrosmectics. The critical field of this transition is

$$H_{ec}^2 = 2\frac{B + K_1 q^2}{\Phi'' v_0} \,. \tag{28}$$

It should be noted, that when $\chi_a < 0$, the parameter Φ'' is positive automatically (see Eqs. (9) and (22)).

(3) $H_e = 0$, $B < 0$: If parameter β, corresponding to magnetic attractions of lyotropic layers, is large enough, the coefficient B in Eq. (25) can be negative. The longitudinal deformations can appear in ferrosmectic in this situation even without magnetic field. The critical value of B for these transformations is

$$B = -K_2 q^2 \,. \tag{29}$$

Hence, besides well-known shear Helfrich deformations, longitudinal deformations can appear in ferrosmectics due to the effect of magnetodipole interparticle interaction. It should be stressed that the value and sign of parameter χ_a of ferrosmectic magnetic anisotropy depends on the ratio l/a_1 of the smectic period to the thickness of the lyotropic layers.

4. Condensation phase transitions

The condensation phase transitions induced by interparticle magnetodipole interactions in ordinary ferrocolloids are well known (see, for example, Refs. [13,17,18]). It is easy to understand, that similar transformations can take place in lamellar ferrocolloids (ferrosmectics). The aim of this point is to study the phase transitions in these systems. To simplify calculations, we assume that the smectic structure of sample is nondeformed now.

Let us denote by $s = \pi a_p^2 n$ the square concentration of the particles in lyotropic layer. Using well-known van der Waals approach, we can estimate the density f_s of steric

free energy of the particles as follows:

$$f_s \approx Tc \ln \frac{s}{1 - s/s_*} , \tag{30}$$

where $s_* \approx \pi/(3\sqrt{3})$ is the maximal square density of the particles in the layer. It is easy to connect the square s, volume ρ and numerical c concentrations of the particles:

$$s = 3\rho \frac{l}{a_{1p}} = 3cv \frac{l}{a_1} . \tag{31}$$

Taking into account (8), (30) and (31), we obtain the following expression for density f of the free energy of the ferroparticles system:

$$f = f_s + f_p = Tc \left[\ln \frac{s}{1 - s/s_*} - \alpha_1^2/6 - sG_1 \right] ,$$

$$G_1 = \frac{G}{4\pi a_p^2} = \gamma^2 \left(1 + \frac{\pi^2}{45} \frac{a_1^4}{l^4} \right) + \gamma \left(\frac{1}{18} (\alpha_{1X}^2 + \alpha_{1Y}^2) + \frac{1}{9} \frac{a_1}{l} \left(2 - \frac{l}{a_1} \right) \alpha_{1Z}^2 \right) . \tag{32}$$

Chemical potential μ and osmotic pressure p of the particles are

$$\mu = \frac{\partial f}{\partial c} = \frac{3l}{a_p} T \left[\ln \frac{s}{1 - s/s_*} + \frac{s}{1 - s/s_*} - 2sG_1 \right] ,$$

$$p = c^2 \frac{\mathrm{d}}{\mathrm{d}c} \left(\frac{f}{c} \right) = \frac{T}{\pi a_p^2 l} \left(\frac{s}{1 - s/s_*} - s^2 G_1 \right) . \tag{33}$$

A simple analysis of relations (33) shows that the van der Waals loops appear on plots of functions $\mu(s)$ and $p(s)$ when parameter G_1 is more than some critical value G_c. It means that the equilibrium separation onto dense and dilute phases can occur in the ferrosmectics. The condition of equilibrium coexistence of these phases is

$$\mu(s_1) = \mu(s_2), \quad p(s_1) = p(s_2) , \tag{34}$$

where indices 1 and 2 correspond to the two coexisting phases. Macroscopical parameter G_1 of the magnetic interparticle interaction depends on microscopical parameter γ. In Fig. 3 the phase diagrams of the phase transition in plane (ρ, γ) are given for different values of ratios l/a_1 and $\alpha_1 = 0$.

Let us discuss the effect of an external magnetic field on the conditions of this phase separation. For simplification we neglect the thin effects connected with diamagnetizing fields and assume that the magnetic fields in the coexisting phases are identical.

The results of calculations of critical value γ_c, corresponding to G_{1c} as a function of the ratio l/a_1 are shown in Fig. 4. It is seen that γ_c increases with the period of the smectic. The physical origin of this result is a decrease of the magnetic interaction between particles inside the different layers with the growth of interlayer distance. The magnetic field parallel to smectic layers decreases γ_c (in other words, it increases a critical temperature of this phase transition); field perpendicular to the layers, decreases γ_c when $l < 2a_1$ and increases it in the opposite case.

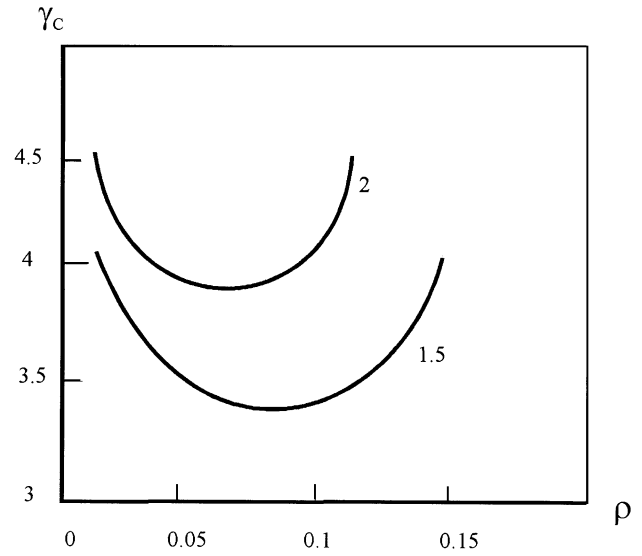

Fig. 3. Phase diagram of the ferroparticles system in the ferrosmectic. Magnetic field is absent. Figures near curves equal to the ratio l/a_1.

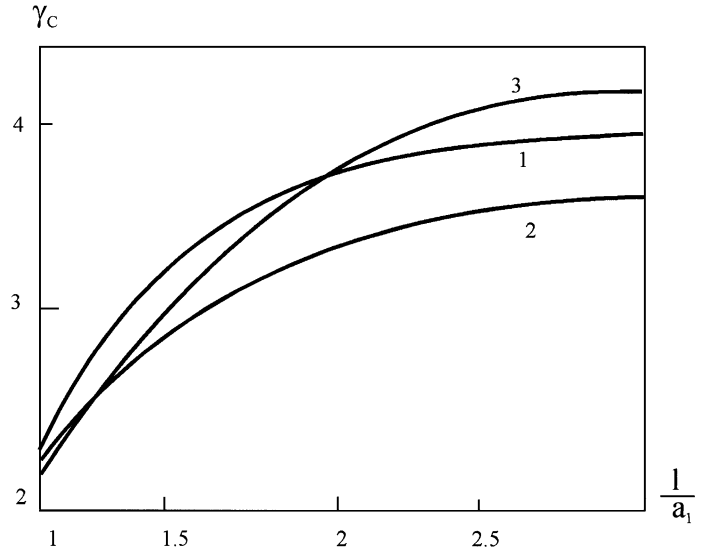

Fig. 4. Dependence of the critical value γ_c of ferroparticles phase separation on ratio l/a_1: (1) $\alpha_1 = 0$; (2) $\alpha_{1X} = 1$, $\alpha_{1Z} = 0$; (3) $\alpha_{1X} = 0, \alpha_{1Z} = 1$.

The dependences of γ_c on α_1 for different orientations of this field and different ratios l/a_1 are presented in Fig. 5.

The particle condensation increases the susceptibility χ_a in regions, where the particle concentration is higher. The smectic structure deformation in these regions can occur

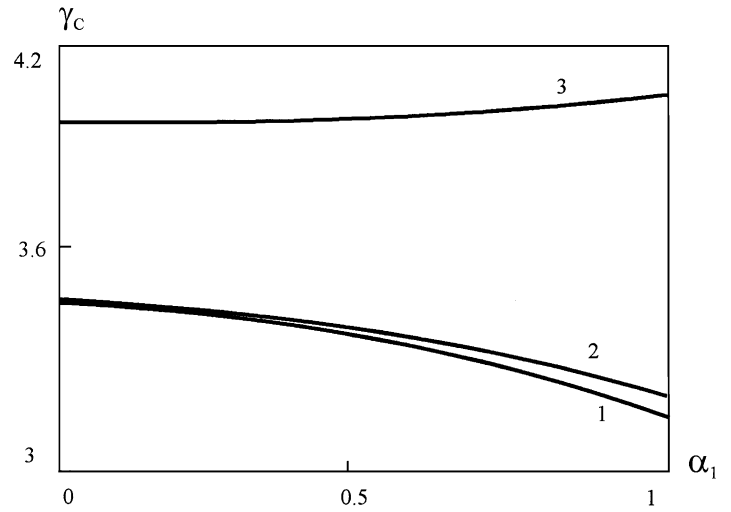

Fig. 5. Dependence of γ_c on a dimensionless magnetic field: (1) $\alpha_1 = \alpha_{1X}$, $l/a_1 = 1.5$; (2) $\alpha_1 = \alpha_{1Z}$, $l/a_1 = 1.5$; (3) $\alpha_1 = \alpha_{1Z}$, $l/a_1 = 2.5$.

more easily as compared to the other parts of the sample. This effect, together with the one studied in Ref. [19], can be the origin of local deformational domains, observed in ferrosmectics in Ref. [6].

5. Conclusions

Thermodynamical characteristics of ferrosmectics are calculated taking into account the magnetic interaction between the particles. Our results show that the initial susceptibility $\chi_{||}$, corresponding to the parallel orientation of a magnetic field to the smectic layers, increases when the interparticle interaction grows. If the field is normal to these layers, then corresponding susceptibility $\chi_\perp$ increases with the interparticle interaction when the thickness a_0 of "water" layer is less than thickness a_1 of the lyotropic layer, containing ferroparticles, and decreases when $a_0 > a_1$. If $a_0 > a_1/3$ then $\chi_a = \chi_{||} - \chi_\perp > 0$ and $\chi_a < 0$ if $a_0 < a_1/3$.

When inequality $\chi_a > 0$ is valid, the Helfrich deformations can occur in ferrosmectic placed in a sufficiently large normal magnetic field. We have estimated the critical values of magnetic field and wave number of the deformations corresponding to the point of the phase transition. When $\chi_a < 0$, some longitudinal deformations can appear in a sufficiently large normal magnetic field. Similar deformations can occur without a magnetic field under the action of magnetic interaction between particles, placed in the different lyotropic layers.

The magnetic interparticle interaction can lead to the condensation phase transition in ferrosmectic and, as a result, to separation of this system from phases with different

concentration of the particles. External field, parallel to smectic layers, increases the critical temperature of this phase transition. The field, normal to the layers, increases this temperature when $a_0 < a_1$ and decreases in the opposite case.

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