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To the theory of phase transitions in layered ferrofluids

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Abstract

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

Ferrosmectics are layered ferrofluids, consisting of smectic liquid crystal with ferromagnetic particles embedded inside the lyotropic layers. These systems were synthesized by Fabre with collaborators and studied actively [1–6]. A phenomenological model of structural deformations in ferrosmectics was suggested in Ref. [7]. As in every phenomenological theory, this model does not allow to calculate macroscopical properties of ferrosmectics on the basis of their microscopical composition. Hence, in spite of the rich experimental material, a consistent theory of these systems is not developed yet. The aim of this work is to develop a statistical theory of ferrosmectics, and, to analyze the structural and condensation phase transitions in these systems.

We suppose that the lyotropic layers, containing ferroparticles, alternate with the layers of low-molecular liquid. Ferroparticles are supposed to be identical spheres with a constant magnetic moment. Particles cannot leave the lyotropic layers. The layer width a is slightly more than diameter d_p of the particle. The magnetic field is assumed weak enough to use linear law of magnetization.

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2. Free energy of the non-deformed sample

The volume density of free energy f_p of ensemble of the particles can be represented as

$$f_p = f_l + f_d. \tag{1}$$

Here f_l is the Langevin free energy of ferromagnetic particle in a magnetic field $\mathbf{H}_l$ internal with respect to the lyotropic layer, f_d is the energy of magnetodipole interaction of the particles. The magnitude f_l can be estimated using the classical Langevin formula: $f_l = -kTc\alpha^2/6$, where c is the number of the particles in a unit volume, $\alpha = mH_l/kT$ (we use the Gauss system of magnetic units), m is the magnetic moment of the particle. We assume that $\alpha < 1$. To estimate f_d we use the regular perturbation theory [8] with respect to the dimensionless parameter $\gamma = m^2/(d_p^3 kT)$ of magnetic interaction of the particles. This theory leads to good agreement with experiments for ordinary magnetic fluids [8,9]. Using mathematically strict considerations of the perturbation theory and assuming that γ is about unity or less, we get

$$f_p = -n\nu kT\left[\frac{\alpha^2}{6} + \rho G\right], \tag{2}$$

$$G = \gamma\left(\frac{l}{3a}(\alpha_x^2 + \alpha_y^2) + \frac{2}{3}\left(2 - \frac{l}{a}\right)\alpha_z^2\right) + gn,$$

$$g = \frac{\pi}{12}\gamma^2 d_p^2\left(1 + \frac{\pi^4}{45}\frac{a^4}{l^4}\right).$$

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Here n is the number of particles per unit square of lyotropic layer, l is period of the smectic structure, $v = 1/l$, ρ is volume concentration of the particles, v is volume of the particle, x, y, z are Cartesian coordinates, the axis z is normal to the smectic layers. Expression (2) allows us to calculate the components of tensor of magnetic susceptibility in the z and x directions:

$$\chi_z = \chi_{\mathrm{L}}(1 + 2\pi\chi_{\mathrm{L}}(2 - l/a)),$$
$$\chi_x = \chi_{\mathrm{L}}(1 + \pi\chi_{\mathrm{L}} l/a),$$
$$\chi_{\mathrm{L}} = \frac{2}{\pi}\rho\gamma, \tag{3}$$

where χ_{L} is the Langevin susceptibility of dilute ferrocolloid. One can see that the value of χ_a as well as its sign depend on the ratio l/a.

3. Structural deformations

Let us assume now that the ferrosmectic undergoes the small inner deformation

$$u = u_0 \cos(qz)\cos(kx). \tag{4}$$

We assume that $u_0 \ll l$, $kl \ll 1$.

In order to study the equilibrium-deformed structure of the system, we determine the total free energy F as a sum of parts, corresponding to magnetic energy of the sample in an external field $\mathbf{H}$, to energy of elastic deformations of the smectic structure and energy of magnetic interaction of the particles without the field. One can find phenomenological expressions for the two first parts of the free energy in any book on liquid crystals (see for example Ref. [10]). These expressions include effective susceptibility of the smectic system, estimated in Eq. (2), and elastic modulus, considered here as empirical magnitudes. The third energy is integral on $kTv(\mathbf{r})\rho(\mathbf{r})g$ over volume of the sample. The magnitudes v and ρ depend on the radius vector $\mathbf{r}$ because of deformation (4). We use Eq. (4) in the expression for F and determine the type of deformations, providing the minimum free energy. The principal part of the minimization procedure is similar to that described in Ref. [10].

Analysis shows that a qualitative picture of deformation phase transitions in ferrosmectics depends on the sign of χ_a as well as on the magnitude $B = C - \beta$, where $\beta = 40kTn^2v_0P$, C is the elastic modulus of deformations of the smectics, corresponding to the term with $(\partial u/\partial z)^2$ in the phenomenogical expression for the elastic free energy (see Ref. [11]), $P = (\pi^5/540)\gamma^2 d_{\mathrm{p}}^2 a^4 v_0^4$, v_0 is v in the non-deformed sample. Calculations lead to the three following situations:

(1) $\chi_a > 0$, $B > 0$ (the elastic modulus is high, the magnetic interaction of the particles is weak). The Helfrich-like deformations can appear in this situation when $H > H_{1\mathrm{c}} \propto \chi_a^{-1/2}$. Because χ_a for ferrosmectics is much more than those for pure liquid crystals, the field $H_{1\mathrm{c}}$ for ferrosmectics is much less than the field of the Helfrich deformations for pure smectic systems.

(2) $\chi_a < 0$, $B > 0$. In this situation a longitudinal deformation ($k = 0$, $q = 2\pi/L$, where $2L$ is the thickness of the sample in the z-direction) must take place when $H > H_{2\mathrm{c}}$. The critical fields $H_{1\mathrm{c}}$ and $H_{2\mathrm{c}}$ are estimated in Ref. [11].

(3) $B < 0$. The longitudinal deformations ($k = 0$, $q = 2\pi/L$) must appear when $|B| > K_2 q^2$. Unlike the two mentioned phase transitions, the last transformation is temperature, not field, induced. The physical origin of the last phase transition is the magnetic attraction of particles from different layers.

4. "Gas–liquid" phase transition

It is well known that condensation "gas–liquid" phase transitions can occur in an ensemble of ferroparticles of ordinary ferrofluids under low temperature or/and external magnetic field. The field stimulates these transformations. Here we study the phase transitions in ferrosmectics. Only equilibrium conditions, not kinetics, of the transition are considered. To simplify calculations, let us assume that the smectic structure of the sample is not deformed. Introducing the square density of the particles in the layer $s = 3\rho\, l/a$, using the classical van-der-Waals estimate for entropy of dense gas of hard spheres, and taking into account Eq. (2), one can write down the following expression for the free energy density:

$$f = kTc\left[\ln\frac{s}{1 - s/s_*} - \frac{\alpha^2}{6} - s\frac{G}{\pi d_{\mathrm{p}}^2}\right]. \tag{5}$$

Here $s_* \approx \pi/(3\sqrt{3})$ is the maximal square concentration of the particles in the layer. Using Eq. (5) one can calculate the chemical potential $\mu(s)$ and osmotic pressure $p(s)$ of the particles. When γ exceeds some critical value γ_{c}, depending on the dimensionless field α inside the lyotropic layers and on the ratio l/a, van der Waals loops appear on the plots of the functions $\mu(s)$ and $p(s)$. It means that "two-dimension gas—two-dimension liquid" phase transition can take place in the ensemble of the particles. The plots of γ_{c} as functions of the ratio l/a for various values and orientations of magnetic field are shown in Fig. 1. Fig. 2 shows the dependences of γ_{c} on the dimensionless field α for various orientations and various values of l/a. The results show that the field, parallel to the smectic layers,

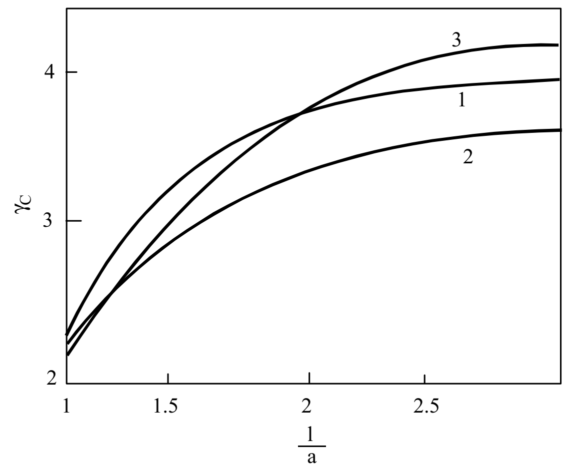

Fig. 1. Dependence of the critical value γ_c of condensation phase transition on the ratio l/a: (1) $\alpha = 0$; (2) $\alpha_x = 1$, $\alpha_z = 0$; (3) $\alpha_x = 0$, $\alpha_z = 1$.

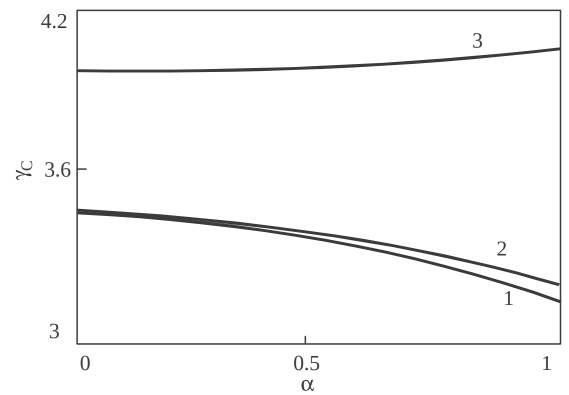

Fig. 2. Dependence of γ_c on the dimensionless magnetic field: (1) $\alpha = \alpha_x$, $l/a = 1.5$; (2) $\alpha = \alpha_z$, $l/a = 1.5$; (3) $\alpha = \alpha_z$, $l/a = 2.5$.

decreases the γ_c, i.e. makes the transition more easy, such as for ordinary ferrofluids. The field normal to the layers, decreases γ_c (induces the phase transition) when the ratio *l/a* is small enough but, in contradiction with ordinary ferrofluids, increases γ_c (prevents the transition) when this ratio is high.

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References

[1] P. Fabre, C. Casagrande, M. Veyssie, Phys. Rev. Lett. 64 (1990) 539.
[2] V. Ponsinet, P. Fabre, M. Veyssie, R. Cabanel, J. Phys. II France 4 (1994) 1758.
[3] V. Ponsinet, P. Fabre, M. Veyssie, Europhys. Lett. 39 (1995) 277.
[4] V. Ponsinet, P. Fabre, J. Phys. II France 6 (1996) 955.
[5] V. Ponsinet, P. Fabre, J. Phys. Chem. 100 (1996) 5035.
[6] V. Cabuil, Proceedings of the 11th Conference of the European Colloid and Interface Society, Lunteren, Netherland, 1997.
[7] A. Cebers, Magnetohydrodynamics 30 (1994) 1.
[8] Yu.A. Buyevich, A.O. Ivanov, Physica A 190 (1992) 276.
[9] A.F. Pshenichnikov, D.B. Yugov, Proceedings of the VIII International Conference on Magnetic Fluids, Timisoara, Romania, 1998.
[10] S. Chandrasekhar, Liquid Crystals, Cambridge University Press, Cambridge, 1977.
[11] A.Yu. Zubarev, A.O. Ivanov, Physica A 291 (2001) 362.