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Condensation phase transitions in ferrofluids

L. Yu. Iskakova, G. A. Smelchakova, and A. Yu. Zubarev
Department of Mathematical Physics, Ural State University, Lenin Av., 51, 620083 Ekaterinburg, Russia

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Experiments show that under suitable conditions magnetic particles in ferrofluids and other polar suspensions undergo condensation phase transitions and form dense liquidlike or solidlike phases. The problem of fundamental features and scenarios of the phase transitions is one of the central problems of the physics of these systems. This work deals with the theoretical study of scenarios of condensation phase transitions in ferrofluids, consisting of identical magnetic particles. Our results show that, unlike the classical condensation phase transitions, the appearance of the linear chains precedes the magnetic particle bulk condensation. The effect of the chains on the diagrams of the equilibrium phase transitions is studied.

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I. INTRODUCTION

Ferrofluids, colloidally stable suspensions of magnetic subdomain particles in a carrier liquid, attract significant interest of researchers and engineers due to their rich set of unique physical properties. The typical size of the particles in modern ferrofluids is about 10–20 nm. In order to prevent coagulation of ferroparticles under the action of colloidal dispersion forces, they are covered with special surfactant or other shells, which screen, partially or completely, colloidal forces. An introduction to ferrofluid science as well as a discussion of their practical applications can be found in [1,2].

Laboratory and computer experiments (see, for example, [3,4]) demonstrate that when the temperature of a ferrofluid is low (however, around the room temperature), and/or the external magnetic field is high enough, magnetic particles condense into linear chainlike or bulk dense drop(column)-like aggregates. The appearance of these aggregates dramatically changes the physical properties of ferrofluids up to several orders of magnitude [2]. That is why the problem of structural transformations and phase transitions in ferrofluids is one of the central problems of the physics of these systems.

Theoretical models of ferroparticle bulk condensation, treated as the classical van der Waals phase transitions in ensembles of single, but interacting magnetic particles, have been suggested in past works [5]. However, many computer (see, for example, [4]) and laboratory [6] experiments demonstrate that thermodynamic equilibrium ensembles of linear chains appear in ferrofluids before the particle bulk condensation. Obviously, the appearance of chains cannot but influence the rate and scenario of the phase transition. Thus the phase transformations in magnetic (dipole) systems have qualitatively new features as compared with the classical transformations in systems with central interactions between particles.

There is intensive discussion (see, for example, Refs. [7]) as to whether a magnetic interaction between particles is able to provide their bulk condensation or the dipole forces can induce only linear "polymerization" of magnetic particles and the central attraction is necessary for their bulk condensation.

Analysis [8] shows that too long chains of dipole particles cannot be thermodynamically stable—they must collapse or condense into dense compact globules. The "gas-liquid" phase transition in a system of dipole particles without central attraction has been observed in computer simulations [9]. These results indicate that the central attraction between dipole particles is not necessary for their bulk condensation. In the model [10] phase condensation of the dipole particles has been treated as a percolation in the system of netlike branched clusters. This scenario, in principle, might be possible; however, it has never been observed in laboratory experiments. Another model of the condensation transition, based on the theory of long polymer chains, has been developed in [11]. From our point of view, specific of the directed dipole interactions between particles as well as the effect of the chain formation on magnetic and sterical interactions between particles, has not been taken into account in this model.

So, in spite of the long story of the problem, even qualitative theory of the phase transitions in magnetic fluids has not been developed yet, and the main question—whether the dipole-dipole interactions can provide the particle bulk condensation, is a subject of many discussions.

In this paper we present the results of theoretical analysis of the condensation phase transitions in an ensemble of magnetic particles. Two limiting cases of zero and infinitely strong external magnetic field are studied.

II. GENERAL MODEL

A majority of modern ferrofluids are polydisperse systems, often with wide distribution over particle size. Here, for maximal simplification of calculations, we consider a system of identical hard magnetic spheres with diameter d and magnetic moment m each. We suppose that d is the total hydrodynamical diameter of the particle, including magnetic core and surface shell. We will take into account that the particles can form linear chainlike clusters and condense into bulk dense phases. It should be noted that various branched and ringlike clusters have been detected in experiments [6] with two-dimensional monolayers of ferrofluids whose thickness was only slightly more than the diameter of the ferroparticle. However, analysis shows that entropy effects are strongly different in two- and three-dimensional systems. In computer simulations with the three-dimensional (3D) systems of dipole particles the chain structures are definitely predominant. That is why we will not consider here the rings and branched structures.

Let us denote by g_n the number of n-particle linear chains per a unit volume of the system. Free energy of the unit volume can be presented as

$$F = kT\sum_{n=1}^{\infty}\left[g_n \ln\frac{g_n v}{e} - g_n \ln Z_n + g_n W_n[g_k]\right]. \qquad (1)$$

Here $v=\pi d^3/6$ is the particle volume. The first term in the brackets of Eq. (1) presents the entropy of ideal gas of the chains. Parameter Z_n is the own statistical integral of the n-particle chain, determined by interactions between particles in the chain as well as fluctuations of their positions and orientations. The magnitude W_n is the dimensionless mean free energy of interaction between the n-particle chain and all other chains (mathematically this free energy is a functional of the distribution function g_n). Thus the second term in left side of Eq. (1) presents the own free energy of the n-particle chain; the third one—the energy of interaction between chains.

The equilibrium distribution function g_n provides a minimum of F under the obvious normalization condition

$$\sum_{n=1}^{\infty} n g_n = \frac{\varphi}{v}, \qquad (2)$$

where φ is the volume concentration of the particles, determined taking into account the surface shells on the particles.

Minimizing Eq. (1) with respect to g_n, taking into account Eq. (2), we get

$$g_n = \frac{1}{v} Z_n \exp\left(-\sum_{k=1}^{\infty}\frac{\delta}{\delta g_n} W_k g_k + \Lambda n\right). \qquad (3)$$

Here Λ is the Lagrange multiplier, and the symbol δ means the variation derivative. In order to calculate the multiplier Λ we must substitute Eq. (3) into condition (2), which leads to an equation with respect to Λ. Having calculated g_n, we can determine the free energy F and then, the chemical potential μ as well as osmotic pressure p of the particles. To this end, we first need to determine Z_n and W_n.

Calculating Z_n, we may take into account only the interaction between nearest particles in the chain. This approximation is supported by the results of laboratory [6] and computer [12] experiments, which are in good agreement with the nearest-neighbor model. In this approximation the statistical integral can be estimated as [13,14]

$$Z_n = \left[\frac{\exp(2\lambda)}{3\lambda^3}\right]^{n-1}, \qquad (4)$$

when $H=0$,

$$Z_n = \left[\frac{\exp(2\lambda)}{3\lambda^2}\right]^{n-1}, \qquad (5)$$

when $H \to \infty$.

III. MEAN ENERGY W_n OF THE CHAIN INTERACTION

Mean dimensionless free energy W_n of the interaction between the n-particle chain and the other chains consists of two parts. The first one is the energy W_n^{st} of the sterical interaction between chains, corresponding to the fact that the chains cannot overlap. The second one is the energy W_n^m of the magnetic interaction between these chains. Therefore we can write

$$W_n = W_n^{st} + W_n^m. \qquad (6)$$

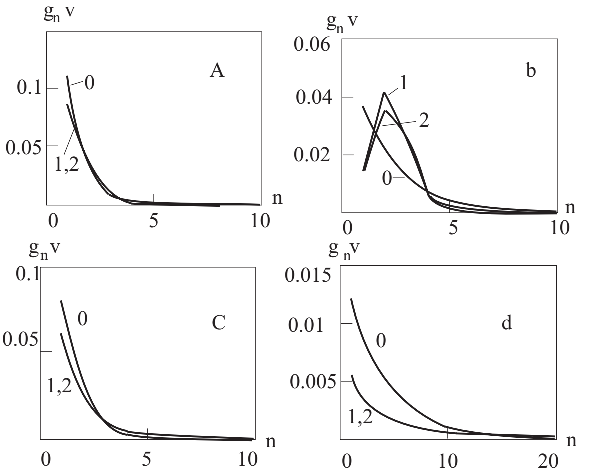

FIG. 1. Distribution function g_n calculated in various iterations $g_n^{(i)}$ (figures near curves—step i of iteration). Volume concentration of particles $\varphi=0.2$. [(a) and (b)] $H=0$. [(c) and (d)] $H\to\infty$. [(a) and (c)] $\lambda=4$. [(b) and (d)] $\lambda=5$.

A. Free energy W_n^{st} of the sterical interaction between chains

In order to estimate W_n^{st}, like in [14], we neglect fluctuations of the chain shape and model n-particle chain by spherocylinder with the length of cylindrical part $n(n-1)d$ and diameter d. Computer [4] and laboratory [6] experiments as well as our calculations (see Figs. 1 and 2) show that the majority of the chains in real ferrofluids are quite short. Since fluctuations of the shape of the short clusters are weak,

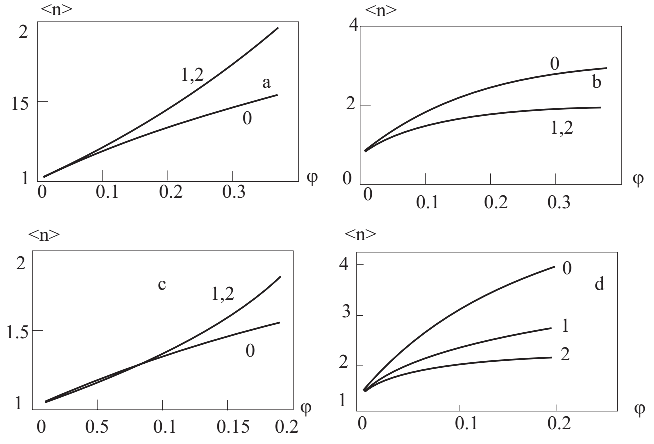

FIG. 2. Mean number of particles in the chain vs particle concentration φ. Figures near curves (a) $\lambda=2$, $H=0$; (b) $\lambda=5$, $H=0$; (c) $\lambda=2$, $H\to\infty$; and (d) $\lambda=4$, $H\to\infty$.

the model of the straight nonfluctuating chain is quite justified, at least, as a first approximation.

When the mean distance between the chains is more than the particle diameter d, which is typical for the "gas" and "liquid" phases, the neglect of details of the "necklace" surface of the chain and modeling it by the cylindrical surface cannot lead to bad errors.

First and foremost we estimate the free energy W_n^{st} in the limit of low concentrations φ. In this case we restrict our consideration to the approximation of the second virial coefficient and analyze the interaction between only two spherocylinders modeling the chains.

In the framework of this approximation the dimensionless free energy W_n^{st} can be presented as

$$W_n^{st}=\sum_k w_{nk}^{st}g_k, \tag{7}$$

where w_{nk}^{st} is the mean mutual excluded volume for n- and k-particle spherocylinders. Let us denote by θ the angle between the axes of these spherocylinders. By using the classical Onsager theory [15] we can present corresponding mutual excluded volume $V_{nk}(\theta)$ in the following form:

$$V_{nk}(\theta)=\left[8+6(n+k-2)+\frac{12}{\pi}(n-1)(k-1)|\sin\theta|\right]v. \tag{8}$$

Let $f(\theta,\psi)$ be the normalized to unity distribution function over mutual orientations of the spherocylinders; ψ is the polar angle. The mean excluded volume is

$$w_{nk}^{st}=\int_0^{2\pi}d\psi\int_0^{\pi}V_{nk}(\theta)f(\theta,\psi)\sin\theta d\theta. \tag{9}$$

It is well known that the spontaneous isotropic medium—nematic phase transition can occur in the system of hard spherocylinders when their length and concentration are high enough. However, this transition has never been observed in the system of chains in ferrofluids. That is why we will assume that without an external magnetic field the spherocylinders have isotropic orientation and

$$f(\theta)=\frac{1}{4\pi},\quad \text{when } H=0. \tag{10}$$

When the field is infinitely strong all model spherocylinders are parallel to the applied field, i.e.,

$$f(\theta)=\frac{1}{2\pi}\delta(\cos\theta-1),\quad \text{when } H\to\infty. \tag{11}$$

Combining Eqs. (10) and (11) with Eqs. (8) and (9), we get

$$w_{nk}^{st}=[8+6(n+k-2)+3(n-1)(k-1)]v, \tag{12}$$

when $H=0$, and

$$w_{nk}^{st}=[8+6(n+k-2)]v, \tag{13}$$

when $H\to\infty$.

It is well known that the approximation of the second virial coefficient with respect to the sterical interaction is not sufficient for the adequate description of the condensation phase transitions. To the best of our knowledge rigorous results for elongated particles have not been obtained even for the third virial coefficient, to say nothing of the higher virial coefficients. Here, like in [14], the free energy of the sterical interaction of a chain with other chains will be estimated in terms of the basic concept underlying the Parsons theory [16]. According to this approach the free energy of the n-particle chain with the other chains can be represented in the form

$$W_n^{st}=\sum_k W_{nk}^{st}g_k,\quad W_{nk}^{st}=w_{nk}^{st}J(\varphi). \tag{14}$$

Expression (14) differs from the relationship (7) only by the factor $J(\varphi)$. Within this approach all information on the shape and mutual orientation of the interacting chains is contained in the reduced sterical energy w_{nk}^{st} of the sterical pair interaction. The effects associated with the multichain interaction are taken into account by the factor $J(\varphi)$, which depends only on the total concentration φ of the particles.

Since the factor J in the Parsons approximation does not depend on the size and orientation of the chains, we can determine it so that for the system of single particles ($n=k=1$) the dimensionless energy W_{11} will coincide with a well-known approximation for a gas of hard spheres. We will use here the Carnagan-Starling approximation, because it leads to very accurate results up to high concentrations of particles. By using the Carnagan-Starling equation of state, one can obtain

$$J(\varphi)=\frac{1-3/4\varphi}{(1-\varphi)^2}. \tag{15}$$

Combining Eqs. (14) and (15) we estimate the sterical free energy as

$$W_n^{st}=\sum_k w_{nk}^{st}g_kJ(\varphi). \tag{16}$$

B. Free energy W_n^m of a magnetic interaction between chains

We estimate the free energy of a magnetic interaction between chains by using an approximation of the second virial coefficient. As a rule, this approximation is quite sufficient for an adequate description of the gas-liquid phase transitions [17].

In the second virial approximation we can present

$$W_n^m=\sum_k W_{nk}^m g_k,$$

$$W_{nk}^m=\int[1-\exp(-U_{nk}(\mathbf{R},\theta,\psi))]f(\theta)d\mathbf{R}\sin\theta d\theta d\psi. \tag{17}$$

Here $\mathbf{R}$ is the radius vector connecting the initial particles in the n-particle and k-particle chains, f is the distribution function over the chain orientations, and U_{nk} is the sum of dimensionless, with respect to kT, potentials of interaction between each particle in the n-particle chain with each particle in the k-particle chain. Calculating U_{nk} we again model the chains as the straight spherocylinders of revolution and assume that the magnetic moment of each particle in a chain is aligned along the chain axis. We should integrate in Eq. (17) in such a way to escape an intersection of the spherocylinders.

The integral in Eq. (17) has defied analytical calculation. Computer calculations of the total integral take too long a time. In order to reduce the time of calculations, we will take into account that the gas-liquid phase transition is expected when the absolute magnitude of U_{nk} is not much more than unity. Indeed, in the case $|U_{nk}| \gg 1$ it is natural to expect the gas-solid transition. In principle, this transition in a system of magnetic particles is possible, however, here we focus on the gas-liquid transformation. That is why we restrict ourselves by the situation when $|U_{nk}| \sim 1$ or a little more.

Assuming that $|U_{nk}| \sim 1$ we expand the exponent in Eq. (17) into the power series with respect to $|U_{nk}|$. In the square approximation we get

$$W^{m}_{nk} = \int U_{nk}(\mathbf{R},\theta,\psi) f(\theta) d\mathbf{R} \sin\theta d\psi - \frac{1}{2}\int U^{2}_{nk}(\mathbf{R},\theta,\psi) f(\theta) d\mathbf{R} \sin\theta d\psi. \tag{18}$$

Analysis shows that in the case of a zero magnetic field the first integral in Eq. (18) equals zero. In the case of an infinitely strong magnetic field this integral has a finite magnitude and, for realistic magnitudes of parameter λ of magnetic interaction between particles, it is significantly more than the second integral, which, therefore, can be neglected. Since $|U_{nk}| \sim \lambda$, we can write

$$W^{m}_{nk} \approx -\lambda \omega^{\infty}_{nk} v, \quad H \to \infty,$$

$$W^{m}_{nk} \approx -\lambda^{2} \omega^{0}_{nk} v, \quad H = 0. \tag{19}$$

Parameters ω^{∞}_{nk} and ω^{0}_{nk} are given in the Appendix.

IV. CHAIN SIZE DISTRIBUTION

Combining Eq. (4) with Eqs. (14) and (17), we get

$$W_{n} = \sum_{k} (W^{st}_{nk} + W^{m}_{nk}) g_{k}. \tag{20}$$

Substituting Eq. (20) into Eq. (3), and taking into account Eqs. (4) and (5), we come to the following equation:

$$g_{n} = \frac{1}{v} X^{n} \exp\left(-\varepsilon_{*} - \sum_{k} (W^{st}_{nk} + W^{m}_{nk}) g_{k}\right)$$

$$\varepsilon_{*} = \frac{1}{n-1} \ln Z_{n}, \quad X = \exp(\varepsilon_{*} + \Lambda). \tag{21}$$

By using estimates (4) we get

$$\varepsilon_{*} = 2\lambda - \ln(3\lambda^{3}), \quad \text{when } H = 0,$$

$$\varepsilon_{*} = 2\lambda - \ln(3\lambda^{2}), \quad \text{when } H \to \infty. \tag{22}$$

Parameter X can be considered as a renormalized Lagrange multiplier. In order to determine X, we must substitute Eq. (21) into the normalization condition (2). It leads to a nonlinear equation of integral type with respect to g_{n}. Equations like that do not have a strict analytical solution. We will solve it by using the method of iterations.

In zero iteration we neglect any interaction between chains, i.e., $W_{n}=0$. By using Eq. (21) one can get

$$g^{(0)}_{n} = \frac{1}{v} X^{n}_{0} \exp(-\varepsilon_{*}). \tag{23}$$

Substituting Eq. (23) into normalization condition (2), we find

$$X_{0} = \frac{1 + y - \sqrt{1+2y}}{y}, \quad y = 2\varphi \exp(\varepsilon_{*}). \tag{24}$$

In the first iteration we use Eq. (23) in the right side of Eq. (21). It gives

$$g^{(1)}_{n} = \frac{1}{v} X^{n}_{1} \exp\left(-\varepsilon_{*} - \sum_{k} (W^{st}_{nk} + W^{m}_{nk}) g^{(0)}_{k}\right). \tag{25}$$

To determine X_{1} we substitute Eq. (25) into Eq. (2). The equation for X_{1} does not have an analytical solution, but it can be solved numerically.

Substituting Eq. (25) into the right side of Eq. (21), we come to the second approximation

$$g^{(2)}_{n} = \frac{1}{v} X^{n}_{2} \exp\left(-\varepsilon_{*} - \sum_{k} (W^{st}_{nk} + W^{m}_{nk}) g^{(1)}_{k}\right). \tag{26}$$

Parameter X_{2} can be determined by substituting Eq. (26) into Eq. (2). This iteration procedure can be continued. One needs to take into account only that the time of calculations increases fast with any new step of iteration.

Some results of calculations of distribution functions g_{n} in zero, first, and second iterations are shown in Fig. 1. One can see that the difference between the first and second iterations is not significant. The third iteration $g^{(3)}_{n}$ (not shown here) nearly coincides with the second iteration g^{2}_{n}, however, it takes much more time for calculation. That is why below we restrict ourselves by the second iteration.

The results presented in Fig. 1 show that for realistic magnitudes of parameters λ and φ the chains are quite short. This result justifies the approximation of straight spherocylinders, used to estimate effects of the chain-chain interaction.

One of the most important characteristics of the chain structure in a ferrofluid is the mean number $\langle n \rangle$ of particles in a chain, which is defined as

$$\langle n \rangle = \frac{\varphi}{v \sum_{n} g_{n}}. \tag{27}$$

Our analysis shows that the sterical interaction between chains increases the mean number $\langle n \rangle$ both in the case of zero and infinitely strong applied magnetic fields. A magnetic interaction between chains decreases their mean size (the re-

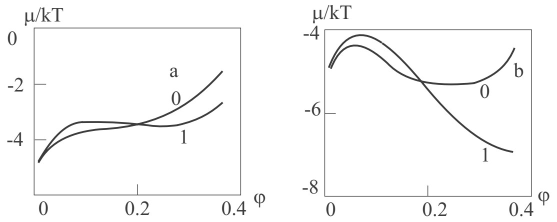

FIG. 3. Chemical potential μ of particles vs their volume concentration φ for the case of zero field when $\lambda = 2.5$ (a) and 3 (b). Numbers near curves—step i of the iteration of calculation of $g_n^{(i)}$.

duction effect of a magnetic interaction is more significant in the case of a strong field than in the case of a weak field). That is why in both cases of zero and infinitely strong magnetic field interaction between chains increases their mean length when λ is relatively small (i.e., the sterical interaction dominates over the magnetic one) and decreases this length when λ is large (magnetic interaction dominates). In the last case the interchain interaction leads to the saturation of $\langle n \rangle$ with the concentration φ. This saturation has been detected in computer simulations [18] but has not been explained theoretically.

V. PHASE TRANSITION

By using Eqs. (20) and (22) we can rewrite the free energy (1) in the following form:

$$F = kT\sum_n \left[g_n \ln\frac{g_n v}{e} - \varepsilon_*(n-1) + \frac{1}{2}\sum_k (W^{st}_{nk} + W^{m}_{nk})g_k \right]. \tag{28}$$

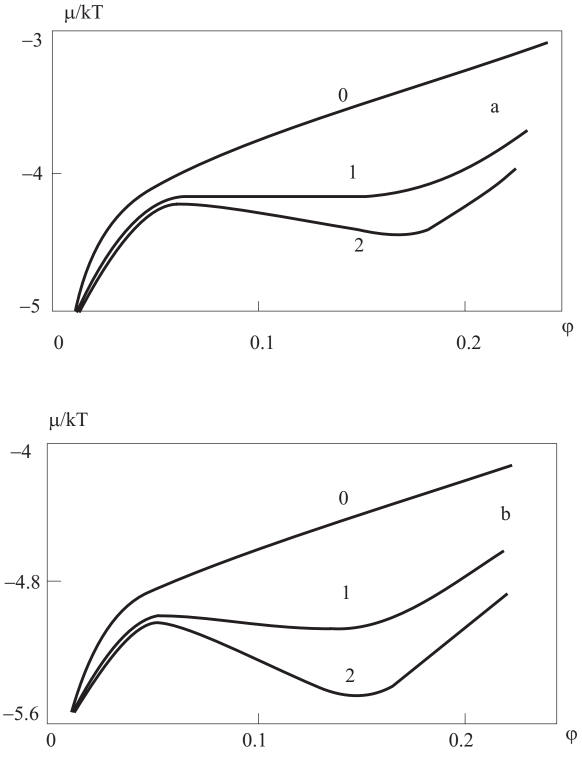

FIG. 4. Chemical potential of particles vs their volume concentration φ for the case of an infinitely strong field when $\lambda = 3$ (a) and $\lambda = 4$ (b). Numbers near curves—step i of the iteration of $g_n^{(i)}$.

Substituting here g_n in one of the approximations (24)–(26), we get the corresponding approximation for the free energy. Having obtained F and by using standard thermodynamical relations, we can calculate the particle chemical potential μ as well as the osmotic pressure p. Some results of our calculations of the chemical potential for the limiting cases of zero and infinitely strong magnetic fields are presented in Figs. 3 and 4. When the dimensionless parameter λ of the chain-chain interaction is strong enough, the van der Waals loops appear on these plots. It means that the gas-liquid phase transitions are possible in these systems. It should be noted that there is an important difference between the situations without a magnetic field and in the strong field. In the first case the van der Waals loops appear in any iteration of calculation of the distribution function g_n, whereas in the case of an infinite field they appear only if the effect of the chain-chain interaction on their size distribution is taken into account.

In the previous works [14] we calculated the chemical potential of ferroparticles in the infinitely strong magnetic field by using zero approximation g_n^0 for the distribution function. On the basis of these results we concluded that in the infinitely strong field the appearance of chains blocks the gas-liquid phase transition, leading rather to the gas-solid transition in an ensemble of the particles. The presented results demonstrate that the reduction of the chain size due to their interaction makes the gas-liquid phase transition possible.

Volume concentrations φ_G and φ_L of the particles in the coexisting gaslike and liquidlike phases can be found from the solution of the following system of equations:

$$\mu(\varphi_G) = \mu(\varphi_L),$$

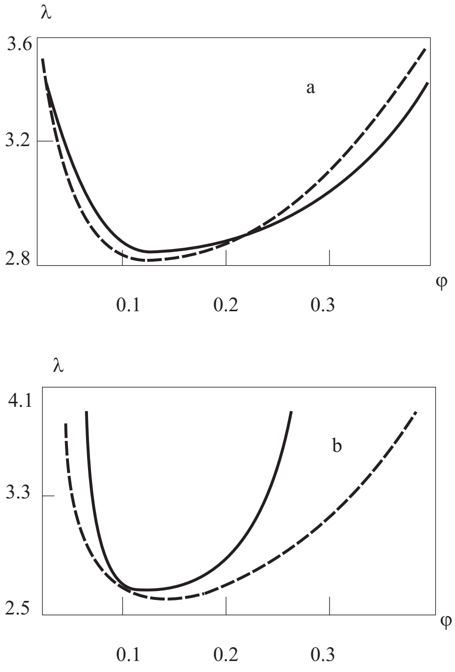

FIG. 5. Diagrams of the equilibrium gas-liquid phase separation without a magnetic field (a) and under an infinitely strong field (b). Solid lines—the presented theory; dashed lines—all particles are considered as single; chains are ignored.

TABLE I. Magnitude of parameter ω_{nk}^{m}.

n/k	1	2	3	4	5	6	7	8	9	10
1	2.511	4.833	6.402	7.551	8.482	9.296	10.041	10.744	11.421	12.078
2	4.833	10.444	15.15	18.72	21.6	24.03	26.22	28.26	30.21	30.21
3	6.402	15.15	22.23	28.92	34.29	38.82	42.81	46.44	46.44	46.44
4	7.551	18.72	28.92	38.28	45	51.96	57.96	57.96	57.96	57.96
5	8.482	21.6	34.29	45	53.13	62.82	71.1	71.1	71.1	71.1
6	9.296	24.03	38.82	51.96	62.82	71.07	71.1	71.1	71.1	71.1
7	10.041	26.22	42.81	57.96	71.1	71.1	71.1	71.1	71.1	71.1
8	10.744	28.26	46.44	57.96	71.1	71.1	71.1	71.1	71.1	71.1
9	11.421	30.21	46.44	57.96	71.1	71.1	71.1	71.1	71.1	71.1
10	12.078	30.21	46.44	57.96	71.1	71.1	71.1	71.1	71.1	71.1

$$p(\varphi_G) = p(\varphi_L). \tag{29}$$

Some results of solutions of the system (29) in the form of standard phase diagrams are presented in Fig. 5. These diagrams demonstrate that, in spite of the chain formation, the gas-liquid phase transition is possible in the systems of ferromagnetic particles. Second, the effect of the chains on the phase diagram of the gas-liquid separation without a magnetic field is insignificant. However, when the field is strong, the appearance of the chains significantly changes the particle concentration in the liquid phase.

It should be noted that the Parsons approximation for the sterical energy W_n^{st} does not influence the qualitative conclusions on character of the phase transitions. The regular second virial approximation for W_n^{st} leads to the same conclusion. The only difference is that in this approximation the increasing right side of the plot of $\mu(\varphi)$ is absent—the function $\mu(\varphi)$ monotonously decreases after a maximum.

VI. CONCLUSION

We present the results of a theoretical study of the scenario of the gas-liquid phase transitions in ferrofluids with subdomain ferromagnetic particles. Only magnetic and sterical interactions between particles are taken into account. Our results show that the linear chainlike aggregates precede the bulk condensation of the particles. However, in spite of the appearance of the chains, the gas-liquid phase separation can take place in an ensemble of the particles due to magnetic interaction between them. The effect of the chains on the phase separation without an external magnetic field is insignificant. This effect must be taken into account if this field is strong.

The sterical interaction between chains increases the mean chain length both in the cases of zero and very strong magnetic field, whereas a magnetic interaction decreases this length. The total reduction effect of the chain-chain interaction significantly influences the condensation phenomena when the applied field is strong.

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APPENDIX

In the framework of approximation (19) for an infinitely strong magnetic field the energy of the magnetic interaction between chains has been calculated in [14]. It was supposed that all chains are parallel to the applied field. We omit details and demonstrate the final result as follows:

$$\omega_{nk}^{\infty} = 12\sum_{i=1}^{n}\sum_{j=1}^{k}\left[S(n-1+j-i)+S(k-1+i-j)\right].$$

Here

$$S(x) = \frac{1}{2}\int_0^1 \frac{\sqrt{1-y}+x}{(1+x^2+2x\sqrt{1-y})^{3/2}}dy.$$

i and j denote particles in n and k particle chains, respectively.

In the case of a zero magnetic field each chain has an arbitrary orientation. The simple considerations of symmetry show that the first integral (18) now equals zero. In order to calculate the second integral we should fix position and orientation one of the chain and integrate over all orientations and positions of the second one in such a way to escape intersection of the spherocylinders that model the chains. It is the same way of integration, which is described in the theory [15], of the sterical interaction between elongated particles. The integral cannot be calculated analytically; the time of numerical calculations at the modern personal computers increases very fast with the numbers n and k. The results for $1 \leqslant n,k \leqslant 10$ are given in Table I. Since the distribution functions g_n decrease fast with n and for the realistic φ and λ the magnitude g_{10} is negligibly small as compared with $g_1,\ldots,g_5$, the restriction by the first ten terms in the sums over numbers n and k of particles in a chain is quite sufficient.

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