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Theory of structural transformations in ferrofluids: Chains and ‘‘gas-liquid’’ phase transitions

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We consider a ferrofluid consisting of identical spherical particles with a permanent magnetic moment. Under the assumption that linear flexible chains can appear in the ferrofluid, we estimate the distribution function of the number of particles inside the chain. The analysis is done and simple expressions for the size distribution function are obtained in asymptotics of a strong magnetic interaction between the particles inside one chain. We studied the influence of the linear chains on conditions and scenarios of bulk ‘‘gas-liquid’’ phase transition in the ensemble of the particles under an infinitely strong magnetic field. In order to study the influence of the chains on bulk ‘‘gas-liquid’’ phase transition in the ensemble of the particles, their chemical potential μ is calculated in the model of separate interacting particles as well as in the model with chains, taking into account the interaction between them. When the temperature is low enough, van der Waals loops appear on the plots of μ versus volume concentration φ of the particles in the first model; function $\mu(\varphi)$ increases monotonically in the second model for all examined temperatures. This means that the condensation ‘‘gas-liquid’’ phase transition can take place in the model of individual particles; however, formation of the chains in real ferrofluids prevents the appearance of this transition.

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I. INTRODUCTION

Ferrofluids are colloidal suspensions of single-domain ferroparticles in a liquid solvent. To prevent agglomeration of the particles under van der Waals forces, they are coated by stabilizing surfactant layers. As a result, only magnetodipole and steric interactions between the particles are significant. Numerous experiments show that, owing to these interactions, various inner microstructures and mesostructures can appear in ferrofluids. These structures strongly affect macroscopic properties of the systems.

Two types of microstructures in ferrofluids are most probable—bulk droplike and linear chainlike aggregates. The bulk ‘‘drops’’ were observed in many experiments (see, for example, Refs. [1–5]). The phenomenon of the appearance of these drops, treated as ‘‘gas-liquid’’ phase transitions in the ensemble of the single particles, has been studied theoretically in Refs. [6–11]. These investigations show that the magnetic field induces the phase transition, and the temperature of the particle condensation under the field is higher than without the field. This conclusion is in agreement with experiments.

Linear ‘‘chains’’ in ferrofluids have been studied theoretically in Ref. [12]. However, in this work analysis of the chains has been performed using known methods of statistical thermodynamics of homogeneous density fluctuations. Only binary correlations between the particles have been taken into account in this model. That is why the structures, studied in Ref. [12], are, rather, ‘‘clouds’’ of the particles, not chains, in the usual sense of the word. The chains, as long, linear aggregates of the closely arranged ferroparticles, have been investigated in Ref. [13]. However, the results of this theory are too cumbersome; it is not a simple problem to use them for applications and generalizations.

A simple model of the chains as straight rodlike aggregates was suggested in Ref. [14]. This model allows us to determine the distribution of the chains over the number of particles inside them, as well as to estimate the influence of the chains on rheological properties of ferrofluids in a wide region of the magnitude of the external magnetic field. However, one needs to admit that the model of the chains as straight rods overestimates both their mean length and their influence on macroscopic properties of ferrofluids. An alternative model of the chains was developed in Ref. [15]. Analysis of the size distribution of the long chains without a magnetic field has been done in Ref. [16] on the basis of the theory of polymer macromolecules consisting of a very high number of monomers. One needs to note that in real ferrofluids the long chains, with the number of particles comparable with those in typical macromolecules, can hardly appear. Moreover, the long polymerlike chains inevitably have a coil-like structure. In these coils the magnetic interaction between the particles, being far from each other along the chain, but closely situated in space, has the same order of magnitude as the interaction between the nearest particles in the chain. Therefore, interaction between the particles far along the chain should play a very important role in the formation of the structure and size distribution of the long polymer-like chains. This circumstance, which was not taken into account in model [16], was recently discussed in Ref. [17].

A qualitative model of the inner phase state in ferrofluids with interacting chains was suggested in Ref. [18]. The model predicts a condensational bulk phase transition in the ferrofluid with chains. However, the results of the model are determined by several phenomenological parameters that are not calculated in the model.

A microscopic study of the influence of the chain-chain interaction on the phase state of ferrofluids has been done in

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Refs. [16–19] on the basis of the model [16] of the chains as long polymer macromolecules. As it was noted, for these very long chains, interaction between the particles, being in one chain and situated far from each other along the chain, plays a very important, (not smaller than the interaction between particles from different chains) role in the formation of the chain structure. However, this interaction of the particles of one chain was not taken into account in these models. Nevertheless, the main conclusions of Refs. [16–19], namely, the fact that the characteristic size of the chain decreases due to the chain-chain interaction and that this interaction prevents the appearance of bulk condensation phase transition, are important. The conclusion that the ''gas-liquid'' phase transition is impossible in the ensemble of the dipole particles was also made in theory [20].

The conclusion that the spatial separation of ferrofluids to two phases with different concentrations of ferroparticles cannot take place and that a decrease in temperature only leads to the formation of more and more long chains in a macroscopically homogeneous system was made in Refs. [21–23] on the basis of the results of numerical simulations. However, one needs to stress that the experiments [1–5] clearly demonstrate the appearance of the bulk droplike aggregates in ferrofluids under low enough temperature and/or a high magnetic field. Therefore there is a contradiction between the laboratory experiments, on one hand, and numerical simulation as well as analytical models that do not ignore appearance of the chains, on the other. The origin of this contradiction is as yet unknown.

Thus the known theories of the inner microstructures in ferrofluids, both linear and bulk ones, cannot answer the question of what the structures correspond to for the given ferrofluid under a given external condition. What appears earlier—the linear chains or the bulk drops? And under what conditions? Since the macroscopic properties of ferrofluids depend strongly on their microscopic structure, the answer to these questions is very important for understanding the physical origin of many phenomena in magnetic fluids.

To solve this problem, it is necessary to develop a microscopic theory of ferrofluids taking into account the possibility of the chains' appearance, and interactions between them as well as between individual particles. Then, on the basis of this model, one can determine the conditions of the bulk ''drop'' formation as a result of the ''gas-liquid'' phase transition in the ensemble of the particles. Study of both these problems is the aim of our work.

The paper is organized as follows. In the first part a simple model of the flexible chains, taking into account the fluctuations of their shape as well as the orientations of magnetic moment of the particles inside the chains, is suggested. Any interactions between the chains are ignored in this part. We restrict our analysis by two limiting cases: (1) the energy of interaction between the nearest particles in one chain is much more than the energy of interaction of the particles with an external magnetic field; (2) the case of inverse relation between these two energies. The point is that, namely, in these limiting situations final results can be obtained using reliable regular mathematical methods.

In the second part of the work we take into account the interaction between the chains and study the influence of the chains on the ''gas-liquid'' phase transition under an infinitely strong magnetic field. The qualitative result of this investigation is that in the model of ferrofluid with chains we did not find van der Waals loops on plots of chemical potential μ of the particles versus their volume concentration φ. This means that the appearance of the chains indeed prevents the condensational ''gas-liquid'' phase transition. However, we cannot exclude that the fact of monotonous dependence of μ on φ is a result of our approximation and think that the intriguing problem of the phase transition in the ensemble of ferroparticles deserves further thorough investigation.

II. DISTRIBUTION OF THE CHAINS OVER THE NUMBER OF PARTICLES

Let us consider a system of identical ferromagnetic spheres of radius a (including the surface layers). We denote by m the magnetic moment of the particle, φ denotes the hydrodynamical volume concentration, and g_n denotes the number of chains in a unit volume of the system. Any interaction between the chains is ignored in this part.

The distribution function g_n is important for our consideration. To determine it we write down the free energy of the unit volume of the ferrofluid as a functional of g_n,

$$F=kT\sum_n \left(g_n \ln\frac{g_n}{e}+g_n f_n\right), \quad e=2.72\ldots. \tag{1}$$

The first term in brackets of Eq. (1) is the entropy of ideal gas of n-particle chains, f_n is dimensionless own free energy of the chain due to its inner structure and interaction with the external magnetic field.

The true function g_n provides a minimum of the functional F under the obvious condition

$$\sum_n n g_n=\frac{\varphi}{v}, \quad v=\frac{4\pi}{3}a^3. \tag{2}$$

The standard calculations give

$$g_n=\exp(-f_n-\lambda n), \tag{3}$$

where λ is the Lagrange multiplier to be determined by substituting Eq. (3) into Eq. (2).

The problem now is to determine f_n. This dimensionless free energy may be presented as

$$f_n=-\ln Z_n,$$

$$Z_n=\int \exp\left[\alpha\sum_{i=1}^{n}\nu_i+\frac{m^2}{kT}\sum_{i=1}^{n-1}\left(3\frac{(\nu_i\mathbf{r}_i)(\nu_{i+1}\mathbf{r}_i)}{r_i^5}-\frac{(\nu_i\nu_{i+1})}{r_i^3}\right)\right]\prod_{j=1}^{n}d\nu_j d\mathbf{r}_j, \tag{4}$$

$$\alpha=\frac{m\mathbf{H}}{kT}.$$

Here ν_i is a unit vector aligned along the magnetic moment of the ith particle in the chain, $\mathbf{r}_i$ is a vector connecting centers of the ith and $(i+1)$th particles. The first term in square brackets of Eq. (4) is the dimensionless energy of interaction of the particles with magnetic field **H**, the second one is the dimensionless energy of magnetic interaction between the particles inside the chain. Only the interaction between nearest neighbors is taken into account here. The problem now is to calculate the many-particle integral (4). We cannot do this in a general case; three typical situations are considered below.

A. Zero field

The statistical integral (4) now is

$$Z_n=\int \exp\left[\frac{m^2}{kT}\sum_{i=1}^{n-1}\left(3\frac{(\nu_i\mathbf{r}_i)(\nu_{i+1}\mathbf{r}_i)}{r_i^5}-\frac{(\nu_i\nu_{i+1})}{r_i^3}\right)\right]\prod_{j=1}^{n} d\nu_j d\mathbf{r}_j . \qquad (5)$$

It is convenient to introduce a local coordinate system with axis Oz aligned along the unit vector ν_i. We may also use the coordinate angles θ, ω, ϕ, and ψ so that

$$\nu_{i+1,z}=\cos\omega,\quad \nu_{i+1,x}=\sin\omega\cos\psi,\quad \nu_{i+1,y}=\sin\omega\sin\psi,$$

$$r_{i,z}=r\cos\theta,\quad r_{i,x}=r\sin\theta\cos\phi,\quad r_{i,y}=r\sin\theta\sin\phi.$$

Using these notations, we have

$$3\frac{(\nu_i\mathbf{r}_i)(\nu_{i+1}\mathbf{r}_i)}{r_i^5}-\frac{(\nu_i\nu_{i+1})}{r_i^3}=\{3\cos\theta[\cos\theta\cos\omega+\sin\theta\sin\omega\cos(\phi-\psi)]-\cos\omega\}\frac{1}{r_i^3}.$$

One can easily see that the integral (5) can be rewritten as

$$Z_n=4\pi\left[\int \exp\left(\gamma\frac{8a^3}{r^3}f(\Omega)\right)r^2 dr d\Omega\right]^{n-1}, \qquad (6)$$

where

$$\gamma=\frac{m^2}{8a^3kT},$$

$$f(\Omega)=3\cos\theta[\cos\theta\cos\omega+\sin\theta\sin\omega\cos(\phi-\psi)]-\cos\omega,$$

$$d\Omega=d\cos\theta d\cos\omega d\phi d\psi.$$

In integral (6) $r\geqslant 2a$, $\phi,\psi\in[0,2\pi]$, $\omega\in[-\pi,\pi]$. At the same time, since, namely, linear chains, not bulk aggregates are considered, we must exclude the close positions of the $(i-1)$th and $(i+1)$th particles and put $\theta\in[0,\pi]$.

The appearance of the chains in ferrofluids is expected only when the dimensionless parameter γ is significantly more than unity. Therefore, the exponent in Eq. (6) decreases rapidly with the increase in distance r between centers of the two neighboring particles. Taking this into account, one can estimate Z_n in Eq. (6) as

$$\begin{aligned}Z_n=Z_{0n}&=4\pi\left[(2a)^3\int d\Omega\int_0^\infty \exp\left(\gamma\frac{f(\Omega)}{(1+\zeta)^3}\right)\times(1+\zeta)^2 d\zeta\right]^{n-1}\\&\approx 4\pi\left[(2a)^3\int \exp[\gamma f(\Omega)]d\Omega\times\int_0^\infty \exp[-3\gamma f(\Omega)\zeta]d\zeta\right]^{n-1}\\&=4\pi\left[(2a)^3\int\frac{\exp[\gamma f(\Omega)]}{3\gamma f(\Omega)}d\Omega\right]^{n-1}, \qquad (7)\end{aligned}$$

where $\zeta=(r/2a)-1$. The symbol 0 at Z_n means that $H=0$.

The function f has a maximum at $\theta=\omega=\phi=\psi=0$. Since γ is assumed to be large, $\exp[\gamma f(\Omega)]$ has a very sharp maximum at this point and rapidly decreases when the angles θ,ω,ϕ,ψ deviate from zero. Thus we can estimate Z_{0n} in the following way:

$$\begin{aligned}Z_{0n}&\approx 4\pi\left[\frac{(2a)^3}{3\gamma f(0)}\int \exp[\gamma f(\Omega)]d\Omega\right]^{n-1}\\&=4\pi\left[\frac{v}{\gamma\pi}\int \exp[\gamma f(\Omega)]d\Omega\right]^{n-1}.\end{aligned}$$

Here we take into account that $f(0)=2$. After manipulations the last integral can be transformed to

$$\int \exp[\gamma f(\Omega)]d\Omega=8(\pi)^2\int_0^1\frac{\sinh(\gamma\sqrt{1+3x^2})}{\gamma\sqrt{1+3x^2}}dx.$$

Finally, we get

$$f_n=-\ln Z_{0n},$$

$$Z_{0n}\approx(4\pi)^n[J_0(\gamma)v]^{n-1},\quad \gamma\gg 1, \qquad (8)$$

$$J_0(\gamma)=\frac{2}{\gamma}\int_0^1\frac{\sinh(\gamma\sqrt{1+3x^2})}{\gamma\sqrt{1+3x^2}}dx.$$

The last integral can be calculated numerically. For applications, the following asymptotic estimate might be convenient:

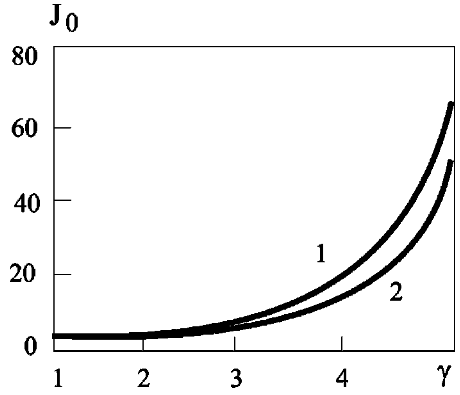

FIG. 1. The numerical calculation of J_0 in Eq. (8) (line 1) and asymptotic estimate (9) (line 2).

$$J_0(\gamma)=\frac{2}{\gamma}\int_0^1 \frac{\sinh(\gamma\sqrt{1+3x^2})}{\gamma\sqrt{1+3x^2}}dx \approx \frac{1}{3}\frac{\exp(2\gamma)}{\gamma^3}, \quad \gamma \gg 1. \tag{9}$$

It should be noted that in approximation (9) our result for the integral in Eq. (6) (which is $J_0 v$ in our notations) coincides with those in Ref. [13].

The comparison of results of the numerical calculation of J_0 in Eq. (8) and asymptotic estimate (9) is shown in Fig. 1. Even for $\gamma=1$ the difference is about 10%.

Substituting Eq. (8) into Eq. (3) and then into Eq. (2), after transformations [14] we get

$$g_n=\frac{1}{v}X^n(\varepsilon_0)\exp(-\varepsilon_0),$$

$$\varepsilon_0=\ln\frac{J_0(\gamma)}{4\pi}, \tag{10}$$

$$X(\varepsilon)=\frac{1+2\varphi\exp(\varepsilon)-\sqrt{1+4\varphi\exp(\varepsilon)}}{2\varphi\exp(\varepsilon)}.$$

Using estimate (9) with logarithmic accuracy, one can obtain

$$\varepsilon_0=2\gamma. \tag{11}$$

Substituting Eq. (11) into Eq. (10) we arrive at the results of Ref. [14], which were obtained by neglecting the fluctuations of the shape of the chains and the orientations of magnetic moments of the particles inside them.

Some results of calculations of the mean number of particles in the chains,

$$\langle n\rangle=\frac{1}{v}\frac{\varphi}{\sum_{n=1}^{\infty} g_n}, \tag{12}$$

are shown in Fig. 2.

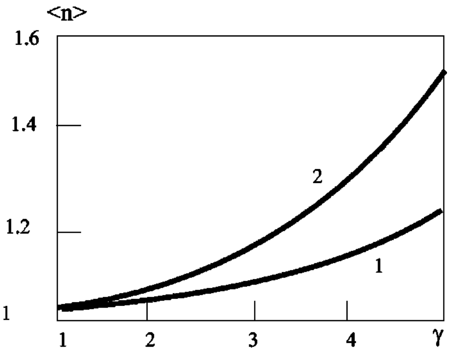

FIG. 2. The mean number $\langle n\rangle$ of particles in the chains for zero field as a function of the dimensionless parameter γ of the magnetic interaction. Curves 1 and 2 correspond to $\varphi=0.05$ and 0.15, respectively.

B. Nonzero weak fields: short chains

Let us now assume that the dimensionless field α is nonzero, but much less than the dimensionless parameter 2γ of the interparticle interaction, i.e., $\alpha \ll \gamma$, $\gamma \gg 1$. Because of the first strong inequality, the second term in square brackets in Eq. (4) varies with the vector ν_i much faster than the first one. Let vector ν_1 be given. Since $\gamma \gg 1$, the exponent in Eq. (4) has a sharp maximum when all vectors ν_i and $\mathbf{r}_i$ are parallel to ν_1. Therefore, the statistical integral Z_n can now be estimated as

$$Z_n \approx Z_{0n}\int \exp[n(\alpha\nu_1)]d\nu_1.$$

After integration over ν_1 we have

$$f_n=-\ln Z_n \approx -\ln\frac{\sinh(\alpha n)}{\alpha n}-\ln Z_{0n}. \tag{13}$$

Substituting Eq. (13) into Eqs. (3) and (2), using results of Ref. [10], we get

$$g_n=Y^n\exp(-\varepsilon_0),$$

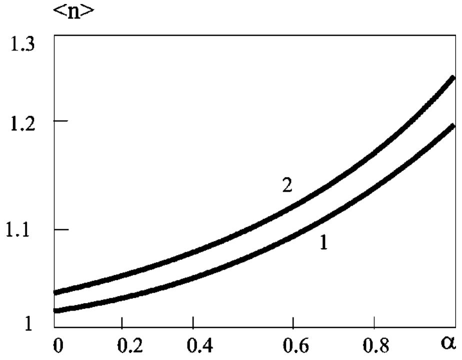

FIG. 3. The mean number $\langle n\rangle$ of particles in the chains vs a dimensionless weak ($\alpha<\gamma$) magnetic field for $\gamma=2$; $\varphi=0.05$ (curve 1) and $\varphi=0.15$ (curve 2).

$$Y=\frac{2y\cosh\alpha+\sinh\alpha-\sqrt{(2y\cosh\alpha+\sinh\alpha)^2-4y^2}}{2y}, \tag{14}$$

$$y=\alpha\varphi\exp(\varepsilon_0),\quad \alpha\ll\gamma,\quad \gamma\gg 1.$$

One can easily see that $Y=X(\varepsilon_0)$ when $\alpha=0$.

The mean number $\langle n\rangle$ of the particles in the chain as a function of the dimensionless field α, calculated with the help of Eqs. (12) and (14), is shown in Fig. 3. One needs to note that the estimate for Z_n and, therefore, relations (13) and (14), are justified only for short enough chains for which fluctuation deviations of the magnetic moment of all particles from the moment of the first one, are small. The criteria, when the restriction is valid, was estimated in Ref. [14] as $\langle n\rangle<2\gamma$. Figure 3 shows that this inequality holds in a wide enough region of volume concentration φ and a dimensionless magnetic field α.

C. Very strong magnetic field ($\alpha\gg\gamma\gg 1$).

Unlike the previous case $\alpha\ll\gamma$, the maximum of the exponent in Eq. (4) now corresponds to identical orientations of all ν_i along the vector α. When vector ν_i deviates from α, the first term in square brackets of the exponent factor varies faster than the second one. Taking this into account and using the same notations as before, we may estimate the statistical integral Z_n for the situation involving a large magnetic field in the following way:

$$Z_{\infty n}=\int\exp\left(\alpha\sum_i\nu_i\right)\prod_i d\nu_i\left[2\pi\int\exp\left(\gamma\frac{8a^3}{r^3}(3\cos^2\theta-1)\right)r^2dr\,d\cos\theta\right]^{n-1}$$
$$=\left(4\pi\frac{\sinh\alpha}{\alpha}\right)^n\left[2\pi\int\exp\left(\gamma\frac{8a^3}{r^3}(3\cos^2\theta-1)\right)r^2dr\,d\cos\theta\right]^{n-1} \tag{15}$$

(symbol ∞ at Z_n means that the field is assumed to be infinitely strong). Repeating the estimates (6) and (7) for the integral over r, we rewrite Eq. (15) as

$$Z_{\infty n}=\left(4\pi\frac{\sinh\alpha}{\alpha}\right)^n J_\infty^{n-1}(\gamma)v^{n-1},$$

$$J_\infty(\gamma)=\frac{2}{\gamma}\int_0^1\exp[\gamma(3\cos^2\theta-1)]d\cos\theta,\quad \gamma\gg 1. \tag{16}$$

For analytical calculations the following asymptotic estimate might be useful:

$$J_\infty\approx\frac{1}{3\gamma^2}\exp(2\gamma). \tag{17}$$

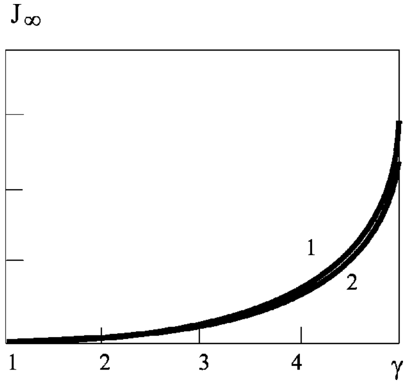

FIG. 4. Calculations of the parameter J_∞ using Eq. (16) (curve 1) and estimate (17) (curve 2).

The accuracy of the estimate (17) is illustrated in Fig. 4.

Using Eq. (17) in Eqs. (3) and (2), after the same calculations as in Ref. [14], we obtain the following expression for the function g_n:

$$g_n=\frac{1}{v}X^n(\varepsilon_\infty)\exp(-\varepsilon_\infty),$$
$$\varepsilon_\infty=\ln J_\infty(\gamma), \tag{18}$$

where X is the same function as in Eq. (10).

The mean number $\langle n\rangle$ of particles in the chain, calculated using Eqs. (12) and (18), is shown in Fig. 5 for the same concentrations φ as in Fig. 2. The comparison of these figures demonstrates the effect of a strong magnetic field on the characteristic length of the chains.

It should be noted that the results (10) and (14) coincide with logarithmic accuracy with those in Ref. [14], obtained by neglecting the thermal fluctuations of the chain structure. Therefore, the model [14] is an upper estimate for the size of the chains. At the same time, the relations (10), (14), and (18) are obtained by neglecting the interaction of all particles in one chain except for the nearest neighbors. The interaction of "far" particles increases the absolute value of the energy of the particle in the chains, hence increasing the average

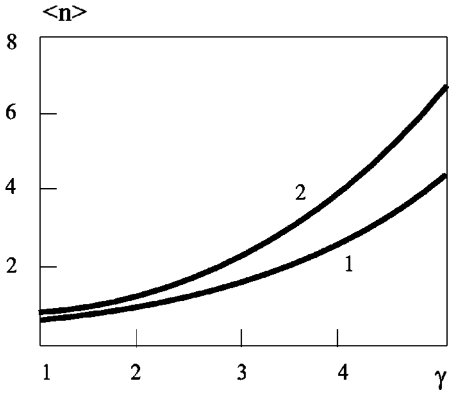

FIG. 5. The mean number of the particles in the chain for an infinitely strong field vs parameter γ for $\varphi=0.05$ (curve 1) and $\varphi=0.15$ (curve 2).

length of the chain. This means that the results, obtained in this part, can be considered as a low estimate for the length of the chain.

Concluding this part, we would like to briefly discuss the difference between our way of calculating the distribution function g_n and those known from literature. As it was mentioned, the first theory [12] of the chains deals with the homogeneous fluctuations of density rather than with the heterogeneous structures considered here. We think that the determination of the distribution function by using the principle of a minimum of free energy is a more direct way of calculating than those based on considerations of chemical kinetics [13–15], though both of them must lead to the same results. Next, the suggested approach, unlike Ref. [16], does not use approximations of the theory of polymer chains that are developed for very long macromolecules, and, therefore, can be used for short or moderately long chains that are expected for real ferrofluids.

III. THE "GAS-LIQUID" PHASE TRANSITION

It was mentioned in the Introduction that bulk "gas-liquid" phase transitions were observed in many experiments with ferrofluids (see, for example, Refs. [1–5]).

The known statistical theories of the transition in Refs. [6–10] deal with the systems consisting only of individual particles, i.e., these models ignore any linear chainlike aggregates. However, numerical experiments [21–24] show that the long enough chains appear in ferrofluids before (instead of) the bulk condensation phenomenon. The aim of this part of the work is to study the problem of equilibrium "gas-liquid" phase transition, taking into account that the chains can appear in the ferrofluid and interact with each other.

The free energy of a unit volume of ferrofluid with interacting chains can be presented in the following form:

$$F=kT\sum_{n}\left(g_n\ln\frac{g_n}{e}+g_nf_n+\frac{1}{2}g_nG_n[g_k]\right). \tag{19}$$

This form differs from Eq. (1) by the presence of the last term with G_n, which is the average energy of interaction of the n-particle chain with the other chains. From a mathematical point of view, this energy is a functional of the distribution function g_k.

To determine the function g_n we should minimize the free energy (19) under condition (2). Unfortunately, this problem cannot be solved strictly because of two fundamental difficulties. First, the exact form for G_n is unknown even for the simplest systems—suspensions of identical spheres. This is connected with the usual problem of statistical physics of dense systems. Second, because of the term G_n, the variation equation $\delta F/\delta g_n=0$ is a nonlinear one of the integral type. Such equations have no exact analytical solutions.

To overcome these fundamental problems and to reach physically clear results, we use the following approximations.

(1) We neglect the influence of the interactions between the chains on the distribution function g_n. Physically, this means that the interaction between the nearest particles in the chains is assumed to be much stronger than the interaction between the chains. Estimates [16] show that this is so at least when the total concentration of the particles is not very high. Mathematically, the neglect of the effect of G_n on g_n means that we may put in Eq. (19) the same function g_n as for noninteracting chains determined above.

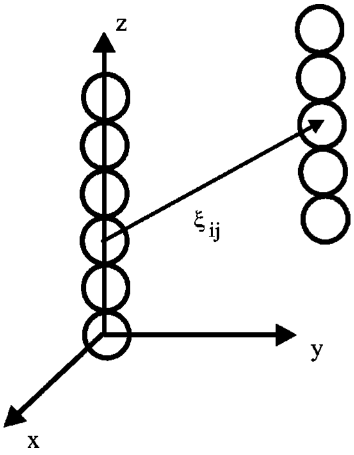

FIG. 6. The Cartesian coordinate system used for calculation of the energy (23).

(2) We consider the interacting chains as straight rods, i.e., we neglect the effect of the thermal fluctuations of their shape on the energy of interaction between them. It is a strong approximation, of course, but it allows us to study the principal results of the chain-chain interaction and to avoid tremendous mathematical problems. It was shown in Ref. [14] that this approximation is justified when the mean number of the particles $\langle n\rangle$ is less than 2γ. Figure 5 demonstrates that this relation is valid in a wide region of the volume concentrations of the particles.

(3) We restrict our analysis by considering the situation of infinitely strong magnetic fields, when all the "rods" are parallel.

(4) To estimate G_n we present it in the form

$$G_n=G_n^m+G_n^{st}, \tag{20}$$

where the upper indices m and st denote the magnetic and steric parts of energy.

First let us estimate the magnetic part G_n^m of the interchain interaction. Using a widely spread model of pair interaction (with respect to magnetic fluids it was used successfully in theory [9]), we may write

$$g_nkTG_n^m[g_k]=g_n\sum_k W_{nk}g_k, \tag{21}$$

where W_{nk} is the average magnetic energy of interaction of two parallel n- and k-particle chains; that is,

$$W_{nk}=-m^2\int\left[\sum_{i=1}^{n}\sum_{j=1}^{k}\left(3\frac{\xi_{ij}^2}{r_{ij}^5}-\frac{1}{r_{ij}^3}\right)\right]dV. \tag{22}$$

Here r_{ij} is the distance between the ith particle in the n-particle chain and jth particle in the k-particle chain, and

ξ_{ij} is the difference between z coordinates of these particles in a coordinate system with the axis Oz aligned along the magnetic field (Fig. 6). Integration in Eq. (22) is held over all positions of, say, the k-particle chain (the n-particle one assumed to be fixed), taking into account that the chains cannot overlap.

Let the origin of the Cartesian coordinate system, shown in Fig. 6, be at the center of the first particle in the first (n-particle) chain, and x,y,z be the coordinates of the first particle in the second (k-particle) chain. Using the approximation of the chains as straight rods, we have

$$W_{nk}=-m^2\sum_{i=1}^{n}\sum_{j=1}^{k}\int\left[\left(3\frac{\xi_{ij}^2}{(\rho^2+\xi_{ij}^2)^{5/2}}\right)-\frac{1}{(\rho^2+\xi_{ij}^2)^{3/2}}\right]dV,$$

$$\xi_{ij}=z+2a(j-i),\quad \rho^2=x^2+y^2. \tag{23}$$

de Gennes and Pincus have shown in Ref. [12] that the integral of type (23) from the potential of the dipole-dipole interaction depends on the shape of the volume of integration. The correct choice of this shape, in the form of an infinitely long cylinder with the axis aligned along the magnetic field, has been used in Ref. [9]. This form of the volume of integration provides correct results since the magnetic field inside this ‘‘cavern of integration’’ coincides with the field outside this ‘‘cavern,’’ i.e., with the macroscopic magnetic field in the place where the two interacting particles are situated.

We are to take into account in integral (23) that the chains cannot interpenetrate. Because of too complex a surface of the chains, the exact form of the excluded volume for these chains is too cumbersome. To get a reasonable estimate we present this excluded volume in the same form as for two spherocylinders with identical radius a and the lengths of the cylindrical part equal to $2a(n-1)$ and $2a(k-1)$, respectively. For these two particles the excluded volume is a spherocylinder of radius $2a$ and the length of the cylindrical part is $2a(n+k-2)$. This approximation for the excluded volume can be used when the mean distance between the axes of the chains is significantly more than $2a$, which is typical of the ‘‘gas’’ and ‘‘liquid’’ states.

Using this approximation we can rewrite the integral in Eq. (23) as

$$\int\left[3\frac{\xi_{ij}^2}{(\rho^2+\xi_{ij}^2)^{5/2}}-\frac{1}{(\rho^2+\xi_{ij}^2)^{3/2}}\right]dV$$
$$=2\pi\left\{\int_{2a}^{\infty}\rho d\rho\left[\int_{-\infty}^{\infty}\left(3\frac{\xi^2}{(\rho^2+\xi^2)^{5/2}}-\frac{1}{(\rho^2+\xi^2)^{3/2}}\right)d\xi\right]\right.$$
$$\left.+S(n-1+j-i)+S(k-1+i-j)\right\}, \tag{24}$$

where

$$S(x)=\int_0^{2a}\rho d\rho\left[\int_{\sqrt{(2a)^2-\rho^2}+2ax}^{\infty}\left(3\frac{\xi^2}{(\rho^2+\xi^2)^{5/2}}-\frac{1}{(\rho^2+\xi^2)^{3/2}}\right)d\xi\right].$$

The integral over ξ is internal and it is to be calculated first. The integral over ρ is external and is to be calculated second. The order of integration is of principal importance here.

One can show that the first integral in square brackets of Eq. (24) equals zero. The function $S(x)$ can be presented as

$$S(x)=\frac{1}{2}\int_0^1\frac{\sqrt{1-y}+x}{(1+x^2+2x\sqrt{1-y})^{3/2}}dy$$
$$=\frac{1}{4x^3}\left[\frac{1}{3}s^{3/2}-2s^{1/2}+(x^4-1)s^{-1/2}\right]\Bigg|_{1+x^2}^{(1+x)^2}. \tag{25}$$

At the integration the following replacement $s=1+x^2+2x\sqrt{1-y}$ has been used. Upper and lower magnitudes for s are given.

After transformations (23)–(25) we have

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

$$W_{nk}=-kT\gamma(2a)^3 2\pi\sum_{i=1}^{n}\sum_{j=1}^{k}[S(n-1+j-i)$$
$$+S(k-1+i-j)]. \tag{26}$$

Now we turn to the estimation of the steric part G_n^{st} of the functional G of interaction between the chains.

If the volume concentration φ of the particles (therefore, chains) is small, we can use the well-known method of virial expansion and restrict ourselves by the approximation of the second virial coefficient. The steric part F^{st} of the free energy F in this approximation can be written as

$$F^{st}=\frac{1}{2}kT\sum_n g_n G_n^{st}=\frac{1}{2}kT\sum_{nk}g_n g_k V_{nk}^{ex}, \tag{27}$$

where V_{nk}^{st} is the excluded volume for the n- and k-particle chains. As is well known, the approximation of the second virial coefficient for the energy of steric interaction is not sufficient to describe the condensation phase transition. The problem is how to generalize Eq. (27) for the concentrated systems. This is one of the unsolved problems in the theory of dense systems of nonspherical particles, which is especially true for the statistical theory of liquid crystals.

Simple, however, successful approximations for F^{st} have been suggested by Parsons in Ref. [25] and used in theories [26,27] of nematiclike systems. According to the idea of Ref. [25], we may present the steric free energy in the following form:

$$F^{st}=\frac{1}{2}kT\sum_{n} g_n G_n^{st}=\frac{1}{2}kT\sum_{nk} g_n g_k V_{nk}^{ex} I(\varphi), \qquad (28)$$

where $I(\varphi)$ is a function only of the concentration φ. Thus, in this model, all information on the shape of these interacting particles is contained only in the excluded volume V_{nk}^{ex}. To estimate the V_{nk}^{ex} we again model the chains as spherocylinders of radius $2a$ and the lengths of the cylindrical parts $2a(n-1)$ and $2a(k-1)$, respectively. Using classical results of the Onsager theory [28] we have

$$V_{nk}^{ex}=6\left(n+k-\frac{2}{3}\right)v. \qquad (29)$$

Since $I(\varphi)$ in the Parsons model does not depend on the shape of the spherocylinders (i.e., neither on n nor k), we can determine this function using known results for F^{st} in a dense system of separate hard spheres. For instance, the classical Carnagan-Starling model gives

$$F^{st}=\frac{1}{2}kTg_1 g_1 v 8\frac{1-\frac{3}{4}\varphi}{(1-\varphi)^2}. \qquad (30)$$

at the same time for the spheres $V_{11}^{ex}=8v$. Comparing Eqs. (28), (29), and (30), one can get

$$I(\varphi)=\frac{1-\frac{3}{4}\varphi}{(1-\varphi)^2}$$

and, therefore,

$$G_n^{st}=6kT\frac{1-\frac{3}{4}\varphi}{(1-\varphi)^2}v\sum_{k}\left(n+k-\frac{2}{3}\right)g_k. \qquad (31)$$

Finally, combining equations (19)–(21), (26), (28), and (31), we obtain

$$F=kT\Sigma_n\left(g_n \ln\frac{g_n}{e}+g_n f_n+\frac{1}{2}g_n\sum_{k} g_k\Phi_{nk}\right),$$

$$\Phi_{nk}=6\left[\frac{1-\frac{3}{4}\varphi}{(1-\varphi)^2}\left(n+k-\frac{2}{3}\right)-\gamma\sum_{i=1}^{n}\sum_{j=1}^{k}[S(n-1+j-i)\right.$$

$$\left.+S(k-1+i-j)]\right]v. \qquad (32)$$

Using Eqs. (32), (15), and (10), we can determine the chemical potential

$$\mu=v\frac{\partial F}{\partial\varphi}=kT\left[-\lambda+\frac{1}{2}\sum_{nk} g_n g_k\left(\frac{2n}{\langle n^2\rangle}\Phi_{nk}+\frac{\partial\Phi_{nk}}{\partial\varphi}\right)\right]v,$$

$$\lambda=\varepsilon_\infty-\ln X(\varepsilon_\infty), \quad \langle n^2\rangle=\sum_{n} n^2 g_n, \qquad (33)$$

and the osmotic pressure of the particles,

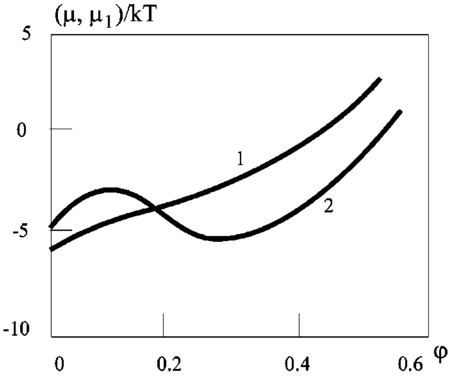

FIG. 7. Chemical potential of the particles in the model with chains (curve 1) and with individual particles only (curve 2) vs volume concentration of the particles; $\gamma=3.5$.

$$p=\frac{\mu\varphi}{v}-F. \qquad (34)$$

To obtain Eq. (33), we use Eq. (3), which gives

$$\frac{\partial g_n}{\partial\varphi}=-n\frac{\partial\lambda}{\partial\varphi}g_n$$

and Eq. (2), which leads to

$$\frac{\partial\lambda}{\partial\varphi}=-\frac{1}{v\langle n^2\rangle}.$$

For comparison, it is useful to give the following expressions for the chemical potential and the osmotic pressure corresponding to the same ferrofluid under the assumption that all particles are separate (any chains are absent):

$$\mu_1=kT\left[\ln\varphi+\varphi\frac{8-9\varphi+3\varphi^2}{(1-\varphi)^3}-8\gamma\varphi\right],$$

$$p_1=kT\frac{\varphi}{v}\left[\frac{1+\varphi+\varphi^2-\varphi^3}{(1-\varphi)^3}-4\gamma\varphi\right]. \qquad (35)$$

Expressions (35) for the chemical potential and the osmotic pressure of the ensemble of individual particles coincide with those following from the mathematically regular theory of perturbations [9] in linear approximation in dimensionless parameter γ of magnetodipole interaction. "Magnetic" parts of Eq. (35) (proportional to γ) also coincide with the relations of mean-field theory [6] for infinitely strong magnetic fields.

Some results of calculations of μ as well as μ_1 are given in Fig. 7. When the parameter γ of the magnetodipole interaction is large enough, the van der Waals loops appear on the plots of $\mu_1(\varphi)$. This means that the "gas-liquid" phase transition is predicted by the model of the individual particles. In contrast, all of our calculations of the function $\mu(\varphi)$ demonstrate monotonically increasing behavior of this function. The mathematical origin of this result is that the "magnetic" term

$$\mu^m = -\gamma\frac{1}{\langle n^2\rangle}\sum_{nkij} g_n g_k n[S(n-1+j-i)+S(k-1+i-j)]$$

of the chemical potential μ in Eqs. (32) and (33) depends on γ nonmonotonically. The absolute value of this term reaches its maximum at $\gamma\approx 2$ and then rapidly decreases. This corresponds to the physical fact that the longer the chains are the weaker the average magnetic interaction between the particles inside the different chains is. For a small γ the $|\mu^m|$ increases with this parameter. However, when γ is large enough, long chains appear in the suspension and play a dominant role in the interparticle interaction. From this moment, the absolute value of μ^m decreases when γ increases and the magnetic attraction of the chains cannot "win" over the combination of steric repulsion and entropy phenomena.

The fact that μ is a monotonously increasing function of the concentration φ shows that the chains prevent the bulk condensation phase transition. At first sight this means that these transitions cannot take place in ferrofluids, which is in qualitative agreement with the results of analytical and computer models [16,19–23]. The principal coincidence of the results of very different analytical models (Ref. [16], Os2, and those suggested here), obtained for different limit cases with respect to the magnetic field (models [16], Os2 are developed for zero field), as well as the results of computer experiments, allow us to think that the main conclusion, namely, that the bulk phase transition is impossible in magnetic fluids, is correct.

However, we cannot affirm with absolute confidence that the "gas-liquid" phase transition is impossible in ferrofluids. Moreover, as it was noted, experiments demonstrate that the transition occurs under suitable conditions. The result that μ is a monotonically increasing function of φ can be an artifact of the following main approximations.

The first is the assumption that the arrangement of the chains is typical of the "dense gas" state and that the average distance between the chains in the transverse direction is more than diameter $2a$ of the particle. Namely, in the framework of this restriction the excluded volume in calculations (24) can be presented in the form of a spherocylinder. In reality, in the dense phase the particles can be packed closely. In the very dense phase the chains lose individuality, therefore their presentation as separate rods is not valid; these highly dense states require special consideration.

Second, strict statistical calculation of the free energy of the system of interacting particles (chains) shows that additional negative terms, proportional to γ^2 and higher powers of γ, must appear in expression (26) for W_{nk} (see, for example, Ref. [9]). When γ is large enough, these terms are, more than those considered here, proportional to γ. One can expect that the terms with γ^n can provide nonmonotonic behavior of μ as a function of φ and describe the condensation phase transition. Analysis of both of the mentioned situations—crystal-like disposition of the particles in the dense phase and the appearance of the terms with $\gamma^2, \gamma^3, \ldots,$ in Eq. (26)— can be the subject of a more advanced theory that we plan to develop in the near future.

Third, the flexible shape of real interacting chains can also increase the effective energy of the magnetic attraction between them, and lead to their condensation.

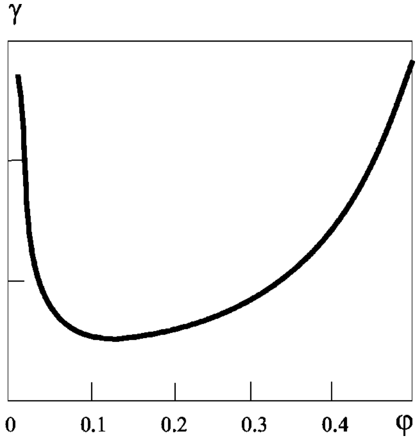

FIG. 8. Binodal curve in the model (35) of the individual particles.

Then, here, as in all works on ferrofluids with chains, we consider a monodisperse system of ferroparticles. However, real magnetic fluids are always polydisperse and there are big particles in them that are able to aggregate. Possibly, the presence of small particles decreases the number of long chains, consisting of big particles, and this creates conditions for the appearance of the bulk phase transition.

Next, tails of the central van der Waals interactions out of the stabilizing layers, coating the particles, can play a decisive role in the condensation phase transitions in real ferrofluids. This fact has been shown in Refs. [27,29].

All of these points require a detailed study. That is why we think that the problem concerning the bulk phase transition in ferrofluids is still open.

The phase diagram (binodal) of the phase transitions, calculated in the model (35) of individual particles, is shown in Fig. 8. As usual this diagram corresponds to the condition

$$\mu_1(\varphi_I)=\mu_1(\varphi_{II}), \quad p_1(\varphi_I)=p_1(\varphi_{II}),$$

where φ_I and φ_{II} are the volume concentrations of the particles in dilute and dense coexisting phases. The critical magnitude of the parameter γ for the condensation transformation is approximately 2.65, and the critical volume concentration φ is about 13%. Since the chains prevent the appearance of the phase separation, the real phase diagram (in the case when the phase transition is possible) lies above the diagram for the model system of individual particles given in Fig. 8.

The mean number $\langle n\rangle$ of the particles in the chains as a function of φ, calculated along the binodal curve, corresponding to model (35) of individual particles, is shown in Fig. 9. On this phase diagram the mean number $\langle n\rangle$ increases very rapidly when φ decreases. This is connected, of course, with the increase of γ on the binodal curve when φ tends to zero. Using this result and taking into account that the chains prevent the bulk phase condensation, and, therefore, the "real" diagram, corresponding to the ferrofluid with chains (if the phase separation in these systems is possible, of

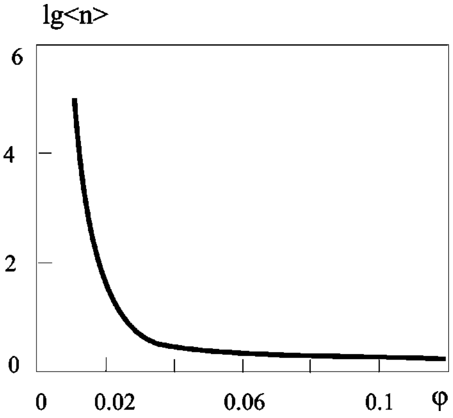

FIG. 9. Mean number of the particles on the binodal curve shown on Fig. 8.

course; we think this problem is still open), one can conclude that when the total concentration of the particles is small (about several percent), long chains appear long before the bulk phase transition. When the concentration is near the critical point $\varphi \approx 0.13$ of the free particles condensation, the phasetransition (if it is possible) can be a condensation of individual particles and short chains.

IV. CONCLUSION

The following two problems are considered. First, the distribution function over the number of particles inside the chainlike aggregate in the ferrofluid is estimated taking into account the thermal fluctuations of the shape of the chains as well as the orientation of the magnetic moments of ferroparticles in the chains. We study two limiting situations: (a) magnetic interaction between the nearest particles in the chains is much stronger than the interaction of the particles with an external magnetic field and (b) the inverse relation between these interactions.

Second, the influence of the linear chains on the equilibrium bulk ‘‘gas-liquid’’ phase transition in the ensemble of the particles under an infinitely strong external field is studied. In the framework of the approximations made, we did not find the conditions of the ‘‘gas-liquid’’ transition in the system with chains. This result is in agreement with Refs. [19–23] where it is concluded that the spatial condensation phase transition is impossible in the systems of identical hard dipole spheres. The qualitative coincidence of the conclusions of several works (ours and Refs. [19–23]), using quite different approaches, allows us to think that this conclusion is true. However, experiments [1–5] clearly demonstrate the bulk ‘‘drops’’ in ferrofluids under suitable conditions. The appearance of these drops and their evolution was described theoretically in Refs. [6–11] under the assumption that any linear chains are absent in ferrofluids. Though these models, in principal points, correspond to experiments [1–5], our consideration shows that the chains cannot be ignored when both the energy of interaction between the particles and their volume concentration are not vanishing, especially if they correspond to the phase diagram in the model of individual particles. Thus there is a qualitative contradiction between experiments, where the bulk ‘‘gas-liquid’’ phase transitions are observed, and theories, both analytical and numerical, where the linear chains in ferrofluids are not ignored. We think that several physical factors, including polydispersity of real ferrofluids and tails of van der Waals interaction beyond the surface layers on particles, can induce the bulk phase separations in these systems. However, we would like to admit that the intrigue of the problem of inner equilibrium phase state of ferrofluids, inner structures, and phase transitions inside of them, is far from being closed and deserves an intensive study.

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