Structural transformations in ferrofluids

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We present results of theoretical study of internal structural transformations in magnetic liquids consisting of identical spherical magnetic particles suspended in a carrier liquid. As the results show, when the dimensionless characteristic energy of magnetic interaction ε between particles is less than a certain critical value ε', the system of particles is in spatially homogeneous state with linear chainlike aggregates. When ε exceeds ε', bulk droplike aggregates, consisting of large number of particles, can occur in this system. The critical parameter ε' decreases when external magnetic field increases. This means that, in accordance with all known experiments, magnetic field stimulates the phase separation. Our estimates of ε' are in agreement with magnitudes of the parameter of interaction between particles in typical ferrofluids where these phase transitions have been observed experimentally. Analysis shows that the bulk dense structures can occur provided that the total number N of particles in the system exceeds a threshold value N', which is about a thousand by order of magnitude. We think that this result explains why the bulk dense clusters, observed in many real experiments, have never been observed in three-dimensional computer simulations of ferrofluids—the total number of particles in these simulations was too small to provide the formation of bulk structures.

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I. INTRODUCTION

Ferrofluids (magnetic liquids, ferrocolloids) are stable colloidal suspensions of fine (about 10 nm in diameter) single-domain ferromagnetic particles in a carrier liquid. To prevent coagulation of the particles under molecular van der Waals forces, they are covered by special polymer layers screening this interaction. The typical thickness of the surface layers is 2–3 nm. As a result only magnetodipole and steric interactions act between the particles. A rich set of unique and valuable, for modern technologies, properties of ferrofluids attracts a rising interest of engineers and investigators to these systems.

Many experiments (see, for example, Refs. [1–8]) demonstrate that ferrofluids exhibit a rich phase behavior as a function of temperature, magnetic field, and physical parameters of the systems. When magnetic interaction between particles is sufficiently strong, they form various bulk droplike aggregates consisting of tremendous, up to several millions, number of the particles. Magnetic field stimulates these transformations and elongates the aggregates along its force lines. Because of tremendous number of particles in these ''drops,'' they can be considered as domains of new dense phase, and their appearance as a first-kind condensation phase transition in the ensemble of the particles.

The first theories of the phase transitions in ferrofluids were suggested in Refs. [9–12]. All these models, being quite different, have a point in common—they treat these phenomena as classical gas-liquid phase transitions in ensembles of interacting, but individual particles. However, many computer experiments (for example, Refs. [13–17]) demonstrate that linear chainlike clusters occur in macroscopically homogeneous systems of magnetic particles long before the bulk phase transitions. In contrast with the laboratory experiments, no bulk aggregates were detected in the majority of three-dimensional computer simulations. We know the only computer model [16] of the systems of dipole particles, which demonstrates some bulklike structures. Analytical models [18,19] demonstrate that appearance of the chains makes the van der Waals-like phase transition in the systems of dipole particles impossible—when temperature decreases, it is more preferable for the chains to grow rather than to condense into the bulk liquidlike phases.

This contradiction between numerous laboratory experiments, on the one hand, and the computer simulations as well as analytical studies of the systems, on the other, opens a question of the fundamental physical reasons for the phase transitions in real ferrofluids.

An idea, suggested in Ref. [18] in order to explain these phenomena, is that there are ''tails'' of the central van der Waals interaction between the colloidal magnetic particles, and, namely, these tails are responsible for the bulk condensation. However, simple estimates show that the typical thickness 2–3 nm of the surface shells on the particles is quite enough to consider the central interaction as being negligible. Thus this interaction can be significant only due to defects of the surface layers. Theoretically these defects can take place, of course. However, quite similar scenarios of the phase transitions have been observed in numerous experiments with various ferrofluids. This fact gives us a background to conclude that the occasional defects of the surface shells cannot be responsible for these phenomena. Moreover, the fact that external magnetic field strongly stimulates the phase transitions shows directly that the dipole interactions play a decisive role in these transformations.

The second reason for the phase transitions can lie in the fact that real ferrofluids are always polydisperse. The smallest particles, almost neutral from the viewpoint of the magnetic interaction, can create entropic depletion forces between the biggest particles, and these interactions might be sufficient to induce the phase transitions. However, in experi-

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ments [8] these transitions have been observed in the systems where the smallest particles were separated from the biggest ones and polydispersity has been strongly reduced. In such conditions the depletion interactions cannot be strong and, therefore, they cannot induce the phase transitions.

Thus, the complex of known experiments provide reasons enough to consider the dipole forces between the particles as being responsible for the bulk condensation phase transitions in magnetic liquids. However, if this is the case, the question arises why the bulk phases have not been observed in computer experiments with dipole particles?

In this work we suggest a scenario of the condensation phase transitions in ferrofluids which takes into account both linear chains and bulk domains of a new phase. The analysis shows that there is a certain critical magnitude ε' of the ratio ε of energy of dipole-dipole interaction between the particles and thermal energy kT of the system. If $\varepsilon<\varepsilon'$, the system is in spatially homogeneous state with chainlike aggregates. If $\varepsilon>\varepsilon'$, the phase transition occurs and the system of particles is separated into dilute and dense phases where the last can be presented in the form of bulk droplike aggregates. In accordance with all known experiments, magnetic field stimulates the phase transition. At the same time our calculations demonstrate that this phase separation can occur provided that the total number N of particles in the system exceeds a certain threshold value N'. This threshold magnitude N' varies from several hundreds to several thousands depending on ε, applied magnetic field and volume concentration of the particles as well. In modern computer simulations of ferrofluids the total number of particles varies just in this region. From our point of view, this result allows us to understand why in three-dimensional computer simulations, in contrast with the laboratory experiments, the bulk drop clusters have not been observed. We think that the number of particles in these numerical experiments was not sufficient to provide the bulk transformations.

II. BASIC MODEL

To simplify the analysis we ignore the polydispersity of ferrofluid and consider a suspension of identical spherical magnetic particles of hydrodynamical (with the surface layers) diameter d, magnetic moment m, and hydrodynamical volume concentration φ. The magnetic interaction between particles is supposed to be strong enough to provide the formation of chainlike and droplike aggregates. We neglect any interaction between different chains or drops. It will be shown below that the last approximation does not influence significantly on the final results.

The free energy of a volume unit of the system can be presented as

$$F=kT\left[\sum_{n=1}^{N}\left(g_n\ln\frac{g_n v}{e}+g_n f_n\right)+\sum_{n=1}^{N}\left(q_n\ln\frac{q_n v}{e}+q_n w_n\right)\right]. \tag{1}$$

Here g_n and q_n are the numbers of n-particle chains and drops in a volume unit of the system, $v=\pi d^3/6$ is the hydrodynamical volume of the particle, and N is the total number of particles in the whole system. For real ferrofluids N may be associated with infinity, whereas in computer experiments N is large, but finite number. The first terms in every sum of Eq. (1) present free energies of the ideal gases of n-particle chains and drops, respectively. The terms f_n and w_n are the dimensionless works of the formation (free energies) of n-particle clusters. Our aim is to determine the distribution functions g_n and q_n and to estimate what part of total number of the particles, under a given condition, is united into the chains and what part into the drops. It would be noted that, for small number of particles in the aggregates ($n=1,2\ldots$), the drops cannot be considered as bulk thermodynamical domains of a new dense phase and for these n the terms in the second sum of Eq. (1) have no physical sense. However, it will be shown below that in real situation the terms with small n in the first sum of Eq. (1) far exceed the corresponding negligible terms of the second sum. Thus the fact that we begin the second sum in Eq. (1) with $n=1$ does not influence on the final results.

The equilibrium distribution functions g_n and q_n provide minimum of the free energy F under the obvious condition of conservation of the total number of particles in the volume unit:

$$\sum_{n=1}^{N} n g_n+\sum_{n=1}^{N} n q_n=\frac{\varphi}{v}. \tag{2}$$

The standard calculations give

$$g_n=\frac{1}{v}\exp(-f_n+\lambda n),\quad q_n=\frac{1}{v}\exp(-w_n+\lambda n), \tag{3}$$

where λ is undefined Lagrange multiplier. Combining Eqs. (3) and (1), one can show that λ is the chemical potential of particles in the system. To determine g_n and q_n, one needs to substitute Eq. (3) into Eq. (2) that leads to a transcendental equation for λ. This equation can be solved numerically.

In order to calculate λ and therefore to determine g_n and q_n, we need to estimate the own dimensionless free energies of the clusters f_n and w_n.

A. The own free energy of the chain

The dimensionless free energy f_n of the n-particle chain can be presented as $f_n=-\ln Z_n$, where Z_n is the statistical integral of the linear cluster. This integral can be calculated by using regular methods of statistical physics only if the applied magnetic field is zero or infinite. For both limiting cases Z_n has been estimated in Ref. [19]. These estimates give the following expression for the dimensionless free energy of the chain:

$$f_n=-(n-1)\varepsilon_{ch}-\kappa n, \tag{4}$$

where

$$\varepsilon_{ch}=\varepsilon-\ln\frac{3\varepsilon^3}{8} \tag{5}$$

for zero magnetic field (the multiplier 4π in denominator of the ratio under the sign of logarithm in Ref. [19] is a mistake of calculations) and

$$\varepsilon_{ch}=\varepsilon-\ln\frac{3\varepsilon^2}{4} \tag{6}$$

for infinite field.

Here and below

$$\varepsilon=\frac{\mu_0}{2\pi}\frac{m^2}{d^3kT},\quad \kappa=\mu_0\frac{mH}{kT},$$

where ε is the dimensionless, with respect to temperature, energy of magnetic interaction of closely situated particles and κ is dimensionless energy of interaction of the particle with the applied magnetic field H. Parameter ε_{ch} is the effective free energy of one particle in a chain due to its interaction with the neighboring particles. This magnitude is determined taking into account thermal fluctuations of positions and orientations of the particles in the chain.

B. The own free energy of the drop

Now let us estimate the free energy w_n of the dense bulk cluster consisting of n magnetic particles. It is important to note that, in contrast to polymer macromolecules which conserve linear structure even in the bulk globule state, in the dense phase of ferrofluid the linear contour of chain must be lost. From topological point of view, this dense phase is a homogeneous fluid of particles rather than dense coil of linear macromolecules. Therefore, to estimate w_n we may use the methods of statistical thermodynamics developed for dense homogeneous ferrofluids.

Classical results of the theory of nucleation [20] and electrodynamics of continuum media [22] give us the following formula for dimensionless minimal work (free energy) of the formation of the bulk cluster:

$$w_n=w_0+w_m+w_s, \tag{7}$$

$$kTw_m=-\mu_0V\int_0^H M_d dH,\quad kTw_s=\sigma S.$$

Here kTw_0 is the free energy of this cluster without magnetic field, V and S are the volume and surface of the drop (globule), M_d is the magnetization inside the drop, σ is the surface tension, kTw_m is the free energy of the cluster induced by the external field H and kTw_s is the surface free energy.

Using the model [12], one can present w_0 and M_d as follows:

$$w_0=w_{hs}(\varphi_d)-n\tfrac{1}{3}\varepsilon^2\varphi_d, \tag{8}$$

$$M_d=m\frac{n}{V}L(\kappa_d)\left(1+4\varepsilon\varphi_d\frac{dL(\kappa_d)}{d\kappa_d}\right),$$

where

$$L(x)=\coth(x)-\frac{1}{x},\quad \varphi_d=\frac{nv}{V},\quad \kappa_d=\mu_0\frac{mH_d}{kT}.$$

Here $L(x)$ is the Langevine function, φ_d is the hydrodynamical volume concentration of particles inside the drop and H_d is the magnetic field inside this aggregate.

The magnitude w_{hs} in Eq. (7) is dimensionless free energy of dense gas of hard spheres with volume concentration φ_d. Let us take into account that, due to the strong magnetodipole interaction, the density of particles inside the globule is expected to be high. Then, in order to estimate w_{hs} we may use the equation of state suggested by Hall in Ref. [22]:

$$p_{hs}=\frac{kT}{v}\varphi_d\frac{A}{\varphi_m-\varphi_d}, \tag{9}$$

where $\varphi_m=0.74$ is the density of close packing of spheres, p_{hs} is the osmotic pressure of gas of these particles and A is a parameter. Using standard thermodynamical relations between the free energy and the pressure, we get

$$w_{hs}=\frac{v}{kT}\int\frac{p_{hs}(\varphi_d)}{\varphi_d^2}d\varphi_d=n\left(\frac{A}{\varphi_m}\ln\frac{\varphi_d}{\varphi_m-\varphi_d}+C\right), \tag{10}$$

where C is a constant of integration. Following Refs. [22,23], the parameters A and C can be determined from condition that gas of hard spheres undergoes entropy driven phase transition with volume concentrations of particles 0.494 and 0.545 for relatively dilute and dense phases, respectively. Using relations (9) and (10) for thermodynamical functions of the dense phase and classical Carnagan-Starling equation for the dilute phase, one can obtain from equations of equalities of osmotic pressures as well as of chemical potentials in these phases that $A\approx 2.2, C\approx 1.255$.

To find the magnetic field H_d inside the globule, we need to determine the shape of this cluster. The exact shape of magnetic drop in nonmagnetic environment is unknown. In a first approximation one may present the aggregate as ellipsoid of revolution with long axis aligned along external field H. As shown in Refs. [5,7], the results of this approximation are in a good agreement with the experimental evidence in weak and moderate magnetic fields. Below we use this ellipsoidal presentation for shape of the globule. Inside homogeneous ellipsoid, the dimensionless magnetic field κ_d is connected with the external one κ by the relation (see in Ref. [21])

$$\kappa_d=\frac{\kappa}{1+\chi_d\xi(c)}, \tag{11}$$

where

$$\chi_d=4\pi\frac{M_d}{H_d}=24\varphi_d\varepsilon\frac{L(\kappa_d)}{\kappa_d}\left(1+4\varphi_d\varepsilon\frac{dL}{d\kappa_d}\right)$$

is the magnetic susceptibility, calculated in model [12], $c<1$ the ratio of minor and major axes of the ellipsoid, $\xi(c)$ the demagnetizing factor which is determined from the following relation [21]:

$$\xi(c)=\frac{c^2}{2(1-c^2)^{3/2}}\left[\ln\frac{1+\sqrt{1-c^2}}{1-\sqrt{1-c^2}}-2\sqrt{1-c^2}\right]. \quad (12)$$

Let us return now to expression (7). The interfacial tension σ between dense and dilute phases of ferrofluid has been estimated in Ref. [24] and can be presented as

$$\sigma\sim\tfrac{1}{2}kT\varphi_d^2 v^{-2/3}G(\varepsilon,\kappa_d), \quad (13)$$

$$G=2\varepsilon L(\kappa_d)^2+\tfrac{1}{3}\varepsilon^2.$$

It should be noted that Eq. (13) is an estimate of the surface tension by the order of magnitude only. However, any exact or precise result for this magnitude has not been obtained theoretically even for relatively simple, for analysis, systems with short-range central interaction between particles. That is why we use here simple approximation (13), which leads to reasonable agreement with experiments, at least by the order of magnitude.

The surface S of the ellipsoidal cluster can be calculated from the well-known formula

$$S=2\pi\left(\frac{3}{4\pi}V\right)^{2/3}\Sigma(c), \quad (14)$$

$$\Sigma=c^{2/3}\left(1+\frac{\arcsin(\sqrt{1-c^2})}{c\sqrt{1-c^2}}\right),$$

Combining Eqs. (7)–(14) and taking into account $V=nv/\varphi_d$, we come to expression for w as a function of φ_d, c and dependent on n,ε, and κ as parameters. To determine φ_d one can use the condition of mechanical equilibrium between the globule and environment. With the help of approximation of zero concentration of particles outside the globule, this condition can be written down as

$$p_d-p_\sigma-p_M=0. \quad (15)$$

Here p_d is the osmotic pressure inside the globule, p_σ is the capillary pressure proportional to σ, p_M is the Maxwell pressure proportional to square of normal component of magnetization. Estimates show that two last terms on the left side of Eq. (15) are smaller than the first one. Therefore, in the first approximation they can be neglected. Using the results of the model [12] and expression (9) for the osmotic pressure of dense gas of hard spheres, one can present p_d in the form

$$p_d=\frac{kT}{v}\left[\varphi_d\frac{A}{\varphi_m-\varphi_d}-\varphi_d^2 G\right]. \quad (16)$$

Thus, the condition $p_d=0$ of mechanical equilibrium between the bulk cluster and empty environment gives

$$\varphi_d=\frac{\varphi_m+\sqrt{\varphi_m^2-4A/G}}{2}. \quad (17)$$

Formula (17) shows that bulk aggregates, being in a mechanical equilibrium with dilute environment, can occur provided that the parameter ε of dipole-dipole interaction between particles is high enough and inequality $G>4A/\varphi_m^2$ holds true.

To determine the form factor c of the ellipsoidal cluster, the condition of minimum of w_n, with respect to c, must be used, i.e.,

$$\frac{\partial w_n}{\partial c}=0. \quad (18)$$

Taking into account Eqs. (11) and (17), representing κ_d and φ_d through κ,ε, and n, the solution of Eq. (18) gives us c as a function of the three last magnitudes. Substituting $c(\kappa,\varepsilon)$ into Eqs. (7) and (8) and keeping in mind Eqs. (9), (10)–(14), and (17), we obtain w_n as a function of n,ε, and κ.

In the general case, the described calculations are not difficult from a principal point of view, but cumbersome. Below we consider two limiting cases with respect to the dimensionless magnetic field : $\kappa=0$ and $\kappa\to\infty$.

Zero field ($\kappa=0$). In this case we have

$$w_m=0,\ \ G=\frac{1}{3}\varepsilon^2,\ \ c=1,\ \ S=4\pi\left(\frac{3}{4\pi}V\right)^{2/3}.$$

Combining these relations with Eqs. (7), (8), and (14), and taking into account that $V=nv/\varphi_d$, we obtain

$$w_n=-n\varepsilon_d+n^{2/3}s, \quad (19)$$

where

$$\varepsilon_d=-w_{hs}+\frac{1}{3}\varepsilon^2\varphi_d,\quad s=\frac{4\pi}{6}\left(\frac{3}{4\pi\varphi_d}\right)^{2/3}\varepsilon^2\varphi_d^2, \quad (20)$$

$$\varphi_d=\frac{\varphi_m+\sqrt{\varphi_m^2-12A/\varepsilon^2}}{2},\quad \kappa=0.$$

Infinitely strong field ($\kappa\to\infty$). The following relations are valid now:

$$G=2\varepsilon+\tfrac{1}{3}\varepsilon^2, \quad (21)$$

$$\kappa_d\approx\kappa\left(1-24\frac{\varphi_d}{\kappa}\xi(c)\right).$$

The form factor c can be determined by using condition (18) of minimum of w_n with respect to this parameter. Substituting Eq. (21) into Eqs. (7), (8), and (14), and taking into account that $\kappa,\kappa_d\gg1$, after simple calculations we get

$$w_n = n\left(\frac{A}{\varphi_m}\ln\frac{\varphi_d}{\varphi_m-\varphi_d}+C-G\varphi_d-\kappa_d\right)$$
$$\times\pi\left(\frac{3n}{4\pi\varphi_d}\right)^{2/3}G\varphi_d^2\Sigma(c). \quad (22)$$

Equation (18) can be presented in the form

$$\frac{\partial w_n}{\partial\kappa_d}\frac{\partial\kappa_d}{\partial c}+\left.\frac{\partial w_n}{\partial c}\right|_{\kappa_d}=0.$$

Combining this equation with Eqs. (21) and (22), in the limit $\kappa,\kappa_d\to\infty$ we come to the following equation for c:

$$\frac{\xi'(c)}{\Sigma'(c)}=-\frac{\pi}{24}\left(\frac{3}{4\pi}\right)^{2/3}G\varphi_d^{1/3}n^{-1/3}, \quad (23)$$

where prime denotes derivation with respect to c. Transcendental equation (23) can be solved numerically. Substituting solution of this equation into Eq. (22), we come to the energy w_n as a function of ε and κ. In the considered asymptotics $\kappa\to\infty$ we may present w_n as

$$w_n=-n\varepsilon_d+n^{2/3}s-n\kappa,$$

where

$$\varepsilon_d=-w_{hs}+G, \quad (24)$$

$$s=\pi\left(\frac{3}{4\pi\varphi_d}\right)^{2/3}\varphi_d^2G\Sigma(c), \quad G=2\varepsilon+\frac{1}{3}\varepsilon^2.$$

III. THE STRUCTURAL STATES OF THE FERROFLUID

Now we are in a position to estimate g_n and q_n. In order to study the influence of magnetic field on the internal structure of the system without cumbersome mathematics, we consider two limiting cases of zero and infinite magnetic field. In both cases the free energies of the particles in the chains and drops can be presented as

$$f_n=-(n-1)\varepsilon_{ch}+n\times\text{const}, \quad (25)$$

$$w_n=-n\varepsilon_d+n^{2/3}s+n\times\text{const}.$$

where $\varepsilon_{ch},\varepsilon_d$ and s are given in Eqs. (5) and (20) for zero field, and in Eqs. (6) and (24) for the infinite one; const is unessential term identical for both functions f_n and w_n.

Let us compare f_n with w_n. As is easily seen, if $\varepsilon_{ch}>\varepsilon_d$, then $f_n<w_n$ for all n. This means that the chainlike state is more preferable for clusters with any number of particles than the droplike state and, therefore, probability of appearance of the drops is very small. The situation is illustrated in Fig. 1(a).

The opposite case, when $\varepsilon_{ch}<\varepsilon_d$, is illustrated in Fig. 1(b). When n is less than a certain critical number n_c, the free energy f_n is below w_n and the linear state for the n-particle cluster is more preferable. Otherwise, when $n>n_c$, the bulk droplike state is more stable. Thus n_c can be considered as a threshold number of particles in the cluster for the chain-drop transformation. The results of calculations of n_c as a function of the dimensionless parameter ε of magnetic interaction between particles are shown in Fig. 2 for both zero and infinite fields.

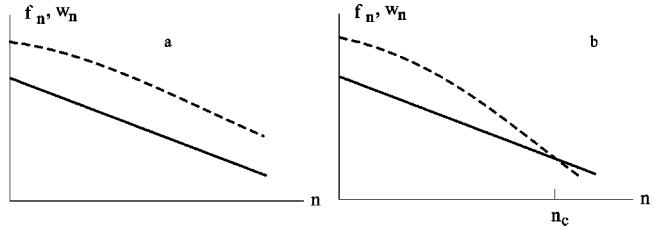

FIG. 1. Illustrations of plots of dimensionless own free energies of chains f_n (solid line) and drop w_n (the dashed one) vs number n of particles in the cluster; (a) $\varepsilon_{ch}>\varepsilon_d$, (b) $\varepsilon_{ch}<\varepsilon_d$.

The result that n_c in infinite field is slightly less than in the zero field, seems to be unexpected since under the field the chain becomes more rigid (ε_{ch} increases). Obviously this factor leads to an increase of n_c. However, at the same time, the dimensionless absolute magnitude ε_d of energy of the particle inside the drop also increases under the field. This factor makes the state of the drop more preferable and decreases n_c. Our results show that in infinite field the second factor dominates. This is possible that in weak but finite fields, the first factor is stronger than the second one and n_c in the field increases. However the case of finite fields requires a separate study.

It should be noted that, in order to avoid very cumbersome mathematics, we have used in calculations of f_n the approximation of nearest neighbors in the chain. At the same time, calculating w_n, we have considered the drops as thermodynamical domains of dense phase with a homogeneous internal structure. As a result we obtained the sharp chain-drop transition at a certain n_c. In the theory of polymer chains, there is a finite region of n for the ''chain-globule'' transformation. Numerical simulations of the chain-globule transitions in the Stockmayer fluids with strong dipole-dipole and weak Lennard-Jones central interaction between soft spherical particles has been done in Ref. [25]. Considering the Lennard-Jones diameter of the soft particle as a diameter

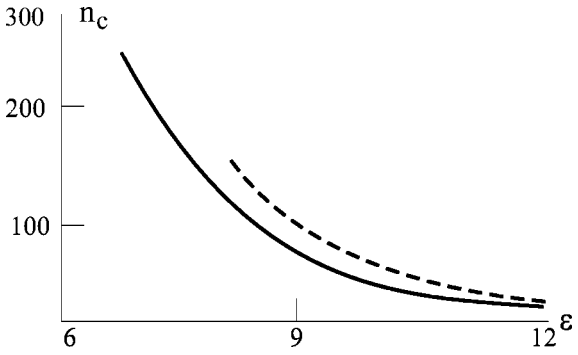

FIG. 2. Dependencies of critical, for the ''chain-drop'' transition, number n_c of particles in cluster on dimensionless energy ε of magnetic interaction between particles. Solid line—infinite magnetic field, dashed one—zero.

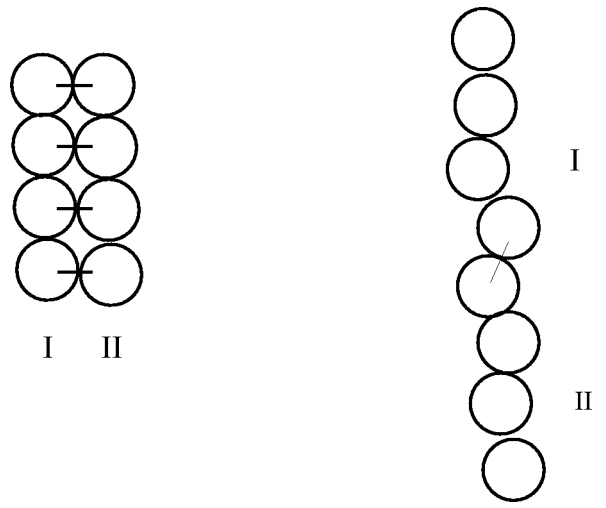

FIG. 3. Two chains united into stripelike and linear clusters. Short lines between particles illustrate magnetic interactions which are taken into account.

of the rigid sphere, for the parameters of the system, used in Ref. [25], with our notation we obtain $\varepsilon \approx 9$. For zero magnetic field and $\varepsilon = 9$ our estimates give $n_c \approx 97$. The computer experiments of Ref. [25] without the field exhibit a transition zone between the chain and globule states which is completed when $n \approx 100-120$. Our estimate $n_c \approx 97$ is close to these magnitudes. Thus, in the first approximation, our simple model is in agreement with the computer experiments.

The inequality $\varepsilon_d > \varepsilon_{ch}$ is fulfilled when the parameter ε exceeds a threshold magnitude ε'. This magnitude must be large enough to provide real values of φ_d in Eq. (17). Direct calculations show that for all ε, providing real values of φ_d, the inequality $\varepsilon_d > \varepsilon_{ch}$ holds true. Thus, we can consider the minimal ε, for which the relation under the square root in Eq. (17) is positive, as the threshold magnitude ε' for a given magnitude of κ. When $\varepsilon < \varepsilon'$, the system is macroscopically homogeneous with chainlike aggregates. When $\varepsilon > \varepsilon'$, the bulk drops of a new phase can appear in the ferrofluid. Our estimates give $\varepsilon' \approx 6.9$ for zero field and $\varepsilon' \approx 4.56$ for the infinite one. The fact that in strong magnetic field the threshold parameter ε' is much less than without the field means that magnetic field stimulates the appearance of the bulk dense phase, and this is in agreement with all known experimental results.

The result that the inequality $\varepsilon_d > \varepsilon_{ch}$, thus $w_n < f_n$ for high n, is fulfilled when ε exceeds a certain critical magnitude ε_c, is not a consequence of concrete statistical estimates of these magnitudes, but follows from general physical considerations. Indeed, consider two n-particle chains in the limiting case of zero temperature when the entropy of the chain and globule is zero. In this case the free energies of these clusters are determined by the energies of particles inside them. We compare absolute magnitudes of energy of attraction of these chains when they form a stripe or the $2n$-particle linear chain. This situation is illustrated in Fig. 3, where I and II are number of the chains.

Let E_1 be the mean magnitude of energy of attraction of particle from the chain I to the chain II. The energy of attraction of these chains in the stripe state in the order of magnitude is nE_1. Consider now chains I and II, united into one $2n$- particle chain and denote by E_2 the absolute value of energy of attraction of two particles at the edges of these chains. In the first approximation E_2 can be considered as energy of attraction of the chains in the linear state. Obviously, $|E_2| > |E_1|$, however when n is high enough, $|nE_1| > |E_2|$. This means that attraction of two short chains is stronger when they form a new chain; attraction between long chains is stronger when they form the stripe or, in three-dimensional case, a bulk cluster. Thus, in the case of zero temperature, for clusters with high enough number of particles $w_n < f_n$. Since these dimensionless free energies are continuous functions of temperature, this means that for low but finite temperatures (i.e., high magnitudes of ε) the inequality $w_n < f_n$ is valid for large n.

Let us turn now to estimates of the parts of total number of the particles united into the chains as well as into the drops. Combining Eqs. (7) and (3), we may present the balance equation (2) as follows:

$$\Phi_{ch} + \Phi_d = \varphi,$$

$$\Phi_{ch} = \exp(-\varepsilon_{ch}) \sum_n^N n \exp[n(\varepsilon_{ch} + \lambda)], \tag{26}$$

$$\Phi_d = \sum_n^N n \exp[n(\varepsilon_d + \lambda) - n^{2/3} s],$$

Here Φ_{ch} and Φ_d are volume concentrations of the particles united into the chains and drops, respectively.

Let $\varepsilon_d + \lambda = -z$, $\varepsilon_d - \varepsilon_{ch} = u$. Using this notation in Eq. (26), we can rewrite the concentrations as

$$\Phi_{ch} = \exp(-\varepsilon_{ch}) \sum_n^N n \exp[-n(u+z)],$$

$$\Phi_d = \sum_n^N n \exp(-nz - n^{2/3} s). \tag{27}$$

Let us suppose, first, that $\varepsilon_{ch} > \varepsilon_d$. In this situation every term in the first sum of Eq. (27) exceeds the term with the same n in the second sum. Calculations show that now for all cases, being of physical interest, the concentration Φ_d is negligible as compared with Φ_{ch}. This means that the probability of appearance of the drops is vanishing and the particles are in single state or united into chains.

Now we study the case when $\varepsilon_{ch} < \varepsilon_d$ (i.e., $\varepsilon > \varepsilon'$) and therefore $u > 0$. Let us suppose that the total number of particles N in the system is large, but finite. Roughly speaking, now the parameter z can be estimated as $z \sim N^{-1} \ln(\varphi/N)$—negative and small, in absolute value,

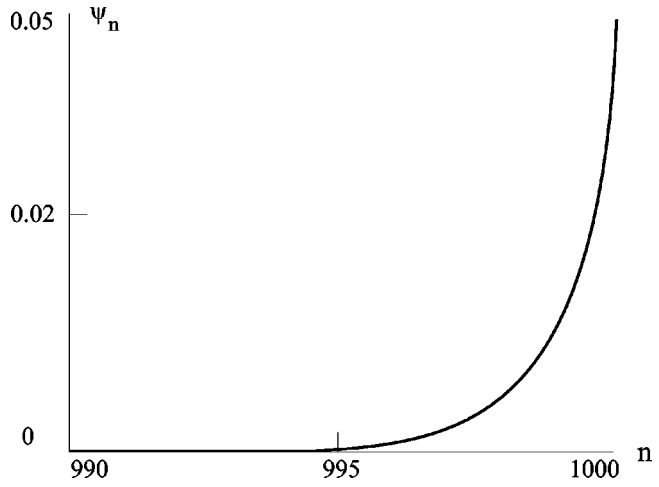

FIG. 4. Results of calculations of volume concentrations ψ_n of particles, united into n-particle drops for $\varphi=0.05$, $N=1000$. Magnetic field is zero.

magnitude. Consider the concentration Φ_{ch} in Eq. (27). Our estimates show that for zero field $u(\varepsilon')=2.65$, for the infinite field $u(\varepsilon')=2.8$. In both cases this function increases fast with ε.

Thus, if ε and therefore u are large, and the absolute magnitude of z is very small, then even the first term in expression for this concentration is negligible as compared with φ (of course, if the last is not too small). Hence, the solution of Eq. (26) is provided by the second term in the left part of this equation. This means that the majority of the particles are collected in the bulk drops. Some results of calculations of the volume concentration $\psi_n=vnq_n$ of the particles united into the n-particle drops are shown in Fig. 4. As seen from the plot, the majority of particles are collected in large drops, whose number is small. Analysis shows that the higher the value of N the sharper increase of this concentration with n. Therefore, in the thermodynamic limit, when N tends to infinity, we have one massive domain of the dense phase in a surrounding medium of single particles. This means that the condensation phase transition takes place. The parameter ε' can be considered as a threshold magnitude of ε, providing the phase transition.

Finishing, we would like to discuss the problem, why the condensation phase transitions, in contrast to numerous laboratory experiments, have not been observed in majority of three-dimensional computer simulations. Our calculations show that if $\varepsilon>\varepsilon'$ (the phase transition can occur), the concentrations Φ_{ch} and Φ_d strongly depend on the upper limit N of the sums in Eq. (26). We remind that this number is equal to the total number of the particles in the system. Some results of calculations of Φ_{ch} and Φ_d as functions of N are shown in Fig. 5. When N is less than a certain magnitude N' depending on ε, φ, and magnetic field, then the number of particles united into the drops is negligible, and the system can be considered as macroscopically homogeneous gas of the single particles and chains. When N significantly exceeds N', the absolute majority of the particles are in the bulk drops. By the order of magnitude N' coincides with total number of particles used in modern computer experiments.

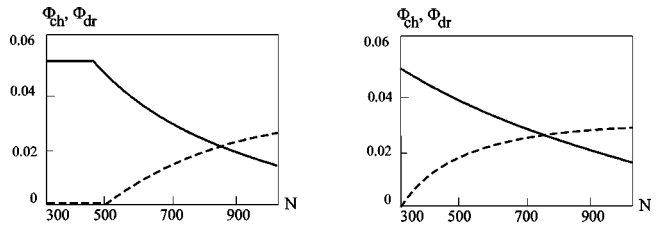

FIG. 5. Dependencies of volume concentrations Φ_{ch} (solid lines) and Φ_{dr} (dashed ones) of the particles, united into the chains and drops, respectively, on the total number N of particles in the system for $\varphi=0.05$; (a) zero field, $\varepsilon=9$; (b) infinite field, $\varepsilon=7.5$.

From our viewpoint, this result allows us to explain, at least qualitatively, the contradiction between computer and laboratory experiments.

IV. CONCLUSION

The structural transformations in the systems of identical magnetic particles are considered. The results show that when the ratio ε of energy of magnetic particle interaction and kT is smaller than a critical value ε', depending on magnetic field, then only chainlike aggregates, not bulk drops, can take place in the system. When ε exceeds ε', the bulk droplike clusters consisting of large number of particles can occur. Appearance of these drops may be considered as the condensation phase transition in the system of the particles.

It should be noted, first, that the conclusion about the occurrence of phase transition in the system of identical magnetic particles at sufficiently large values of parameter ε is not a result of concrete statistical estimates of the thermodynamical magnitudes of the system. This is a direct consequence of the fact that ground state of the many-particle cluster is bulk, not linear. Second, our approximation of the noninteracting clusters cannot significantly influence on the results of presented analysis. Indeed, the interaction between different clusters must be weaker than the interaction between the particles inside one cluster, otherwise these clusters would be united into one aggregate. Thus the cluster-cluster interaction cannot significantly influence on the equilibrium thermodynamical state of the system.

Let us discuss now our estimates of ε'. For zero and infinite magnetic fields they are 6.9 and 4.564, respectively. One can show that in typical magnetite ferrofluids with the thickness of the surface layers on the particles of about 3 nm, at room temperatures these magnitudes of ε correspond to diameter of the particles in the range 16–18 nm. The particles of these sizes are always in real ferrofluids, therefore they can condensate into droplike domains of new phase. Thus our estimates of the critical magnitude of ε are in agreement with the results of observations of phase transitions in ferrofluids.

Our analysis shows that the bulk structures can appear in the system of magnetic particles provided that their total number N is large enough. We think that this result reflects the well-known result of the theory of phase transition—only

large enough, overcritical nuclei of new (dense) phase in a metastable system can be viable. When N is too small, no overcritical drops can appear in the system. From our point of view, it allows us to explain why the bulk drops of magnetic particles have not been observed in many computer experiments—the total number of particles in these simulations was too small to form the viable overcritical drops.

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