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Effect of interaction between chains on their size distribution: Strong magnetic field

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We consider ferrofluid consisting of identical spherical particles with permanent magnetic moment. Under the assumption that linear chains can appear in the ferrofluid, we estimate the distribution function of a number of the particles inside the chains. The main new moment of our consideration is that we estimate the influence of interaction between the chains on the size distribution as well as on the mean number of the particles in the chain. The analysis is done and simple expressions for an the size distribution function are obtained for infinitely strong magnetic field in asymptotics of strong magnetic interaction between the particles inside one chain.

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I. INTRODUCTION

Ferrofluids (magnetic fluids, ferrocolloids) are colloidal suspensions of single-domain ferroparticles with permanent magnetic moment in a carrier liquid. 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. Many experiments show that under the dipole-dipole interaction, the particles can agglomerate into linear chainlike aggregates (see, for example, [1] and references therein). These chains can influence macroscopical, especially rheological, properties of the systems very strongly [1,2].

Many models of the chainlike structures in ferrofluids [2–5] ignore effects of interaction between the chains as well as between them and free particles. However it is known that these interactions can lead to the appearance of bulk droplike aggregates in magnetic fluids [6–9]. Theories of these bulk transformations [10–13] treat them a as ‘‘gas-liquid’’ phase transition in the ensemble of single particles. At the same time numerical experiments [14–18] demonstrate that formation of long chains can take place before and even instead of the bulk condensation phenomena. The appearance of long linear chains before bulk aggregates was observed also in magnetorheological fluids—suspensions of paramagnetic particles with magnetic moment induced by the external field [19]. Therefore, the chains and interactions between them play an important, often decisive, role in the formation of inner structure and phase state in magnetic fluids.

Theoretical analysis of the influence of chain-chain interaction on their size distribution and the ‘‘gas-liquid’’ phase transition in ferrofluids without magnetic field has been done in Refs. [20]. However, these models are based on a mathematical technique of theory of long polymer chains with very high number of monomers. In real ferrofluids the chains with a number of particles comparable with those of monomers in typical polymer macromolecules are hardly expected.

One needs to note that mean diameter of ferroparticles in typical ferrofluids is about 10 nm. Estimates show that magnetic interaction between these small particles is too weak to provide any agglomeration phenomena. But real ferrofluids are always polydisperse and the biggest particles with diameter a about 15–20 nm take place in these systems. These big particles can unite into linear and bulk aggregates. In many typical ferrofluids concentration of the big particles is high enough for formation of various micro- and mesoclusters. Recently special experiments on the creation of ferrofluids with high concentration of the big particles are carried out successfully [21]. For these systems probability of the associate phenomena are especially high and, therefore, the study of formation of various clusters is especially actual.

The aim of this work is theoretical analysis of the influence of the effect of chain-chain interaction on equilibrium size distribution of linear chains in ferrofluids, placed into an infinitely strong magnetic field. We assume that the chains are not very long, therefore thermal fluctuations of their shape are small and the interaction between far (along the chain counter) particles is not significant. For maximal simplification of calculations, we consider monodisperse system, consisting of big enough particles, capable of forming heterogeneous structures. With respect to real polydisperse systems this means that we ignore the influence of small particles on the chain structure. Analysis of this influence can be a next step the in study of internal structures in ferrofluids.

II. FREE ENERGY DENSITY OF THE FERROFLUID

Consider a system of identical spherical particles with hydrodynamical (with surface layers) radius a and permanent magnetic moment m suspended in a carrier liquid. Let g_n be a number of the n-particle chains in a unit volume of the magnetic liquid. Free energy of the particles in the unit volume can be presented in the following form:

$$F=kT\sum_{n=1}\left(g_n\ln\frac{g_n v}{e}+g_n f_n+g_n G_n[g_k]\right), \tag{1}$$

$$e=2.72\ldots .$$

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Here f_n is dimensionless “own” free energy of the chain due to interaction of the particles inside it and their interaction with magnetic field H, v is volume of the particle, which is considered here and below as an elementary phase volume. The magnitude G_n is the average dimensionless free energy of the interaction of the n-particle chain with the others, including free particles. From a mathematical point of view G_n is a functional of the distribution function g_n.

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

$$\sum_n n g_n = c = \frac{\varphi}{v}, \tag{2}$$

where c is a total number of the particles in the unit volume, and φ is their volume concentration. Our aim is to find the function g_n. To do this we need, first of all, to determine the dimensionless free energies f_n and G_n.

III. THE “OWN” FREE ENERGY OF THE CHAIN

The dimensionless free energy f_n can be presented in the following form:

$$f_n = -\ln Z_n,$$

$$\begin{aligned} Z_n = (2a)^{3(n-1)} \int \exp\Bigg[\left(\alpha \sum_{i=1}^{n} \nu_i \right) \\ + \gamma \sum_{i=1}^{n-1} \left(3 \frac{(\nu_i \cdot \mathbf{r}_i)(\nu_{i+1} \cdot \mathbf{r}_i)}{r_i^5} - \frac{(\nu_i \cdot \nu_{i+1})}{r_i^3} \right) \Bigg] \prod_{j=1}^{n} d\nu_j d\frac{\mathbf{r}_j}{v}, \end{aligned} \tag{3}$$

$$\alpha = \mu_0 \frac{m\mathbf{H}}{kT}, \quad \gamma = \frac{\mu_0}{4\pi} \frac{m^2}{8a^3 kT}, \quad \mathbf{r}_i = \frac{\mathbf{R}_i}{2a}.$$

Here ν_i is a unit vector aligned along a magnetic moment of ith particle in the chain, and $\mathbf{R}_i$ is a vector, connecting centers of the ith and $(i+1)$th particles. The first term in the square brackets of Eq. (4) is dimensionless energy of interaction between the the particles and magnetic field $\mathbf{H}$, and the second one is dimensionless energy of magnetic interaction between the particles inside the chain. The interaction between only nearest neighbors is taken into account here. It should be noted that this approximation is more precise the longer the chain is. The problem now is to calculate the many-particle integral (3). We cannot do it a in general case and consider a situation when the magnetic field is infinitely strong. At the same time the appearance of the chains is expected only when the dimensionless parameter γ of magnetic interaction of the particles is significantly more than unity. The situation that we consider is $\alpha \gg \gamma \gg 1$.

It is convenient to introduce the local coordinate system with axis Oz aligned along the field. The exponent under the integral in Eq. (3) has sharp maximum when all vectors ν_i and $\mathbf{r}_i$ have only z components. Since the following strong inequality $\alpha \gg \gamma \gg 1$ is assumed, the first term in the exponent in Eq. (3) changes faster than the second one when ν_i deviates from the axis. Therefore in the asymptotics $\alpha \to \infty$ the statistical integral (3) can be rewritten as

$$\begin{aligned} Z &= \left(\frac{(2a)^3}{v} \right) (n-1) \int \exp\left(\alpha \sum_i \nu_i \right) \prod_i d\nu_i \\ &\quad \times \left[2\pi \int \exp\left(\gamma \frac{1}{r^3} (3\cos^2\theta - 1) \right) r^2 dr\, d\cos\theta \right]^{n-1} \\ &= \left(\frac{(2a)^3}{v} \right) (n-1) \left(4\pi \frac{\sinh\alpha}{\alpha} \right)^n \\ &\quad \times \left[2\pi \int \exp\left(\gamma \frac{8a^3}{r^3} (3\cos^2\theta - 1) \right) r^2 dr\, d\cos\theta \right]^{n-1}, \end{aligned} \tag{4}$$

where $r_z = r\cos\theta$. Taking into account that the parameter γ is assumed to be more than unity, we can use the following asymptotic estimate for the integral over r:

$$\begin{aligned} \int_{r>1} \exp\left(\frac{\gamma P(\theta)}{r^3} \right) r^2 dr &= \frac{1}{3} \int_{r>1} \exp\left(\frac{\gamma P(\theta)}{y} \right) dy \\ &= \frac{1}{3} \int_{s>0} \exp\left(\frac{\gamma P(\theta)}{1+s} \right) ds \\ &\approx \frac{1}{3} \int_0^\infty \exp(\gamma P(\theta)(1-s)) ds \\ &= \frac{1}{3\gamma P(\theta)} \exp(\gamma P(\theta)). \end{aligned} \tag{5}$$

Substituting this estimate into Eq. (4), taking into account that for large γ the exponent in Eq. (5) has a sharp maximum at $\theta = 0$ and varies with the angle θ much faster than the preexponent multiplier, we obtain approximately

$$Z_n = \left(4\pi \frac{\sinh\alpha}{\alpha} \right)^n J^{n-1}(\gamma) v^{n-1}, \tag{6}$$

$$J(\gamma) = \frac{2}{\gamma} \int_0^1 \exp(\gamma(3\cos^2\theta - 1)) d\cos\theta, \quad \gamma \gg 1.$$

For analytical calculations the following asymptotic estimate might be useful:

$$J \approx \frac{1}{3\gamma^2} \exp(2\gamma). \tag{7}$$

The same asymptotic estimate has been obtained in Ref. [4].

The accuracy of the estimate (7) is illustrated in Fig. 1. Even for γ close to unity the difference between numerical calculation of the integral in Eq. (6) and estimate (7) is relatively small.

Thus, when $\alpha \gg \gamma \gg 1$ we come to the following asymptotic relation:

$$f_n = -[\alpha n + (n-1)\ln(J)]. \tag{8}$$

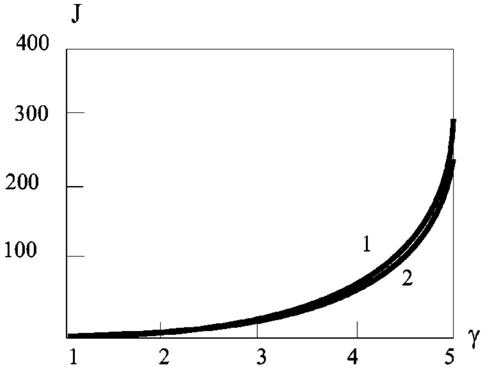

FIG. 1. Numerical calculation of the parameter J in Eq. (6) (curve 1) and analytical estimate (7) (curve 2).

In conclusion of this part we would like to note that explicit magnitude of the elementary phase volume in Eqs. (1) and (3) does not influence the final physical result. Our choice of the this volume as volume v of particle makes all calculations shorter.

IV. THE AVERAGE ENERGY OF INTERCHAIN INTERACTION

To estimate G_n we present it in the form

$$G_n = G_n^m + G_n^{st}, \tag{9}$$

where the upper indexes m and st stand for magnetic and steric parts of the energy. For maximal simplification of the mathematical side of the problem, we now treat the interacting chains as straight rodlike aggregates. In the other words, we suppose that the characteristic size of the chain along the field is much more than those in the transversal direction. This idealization is strong, especially for long enough chains, however, it allows us to reach physically reasonable estimates and qualitatively important results without very cumbersome mathematics.

First, let us estimate the magnetic part G_n^m of the interchain interaction. Using the widely spread model of pair interaction (with respect to magnetic fluids it was successfully used in theory [13]), we may write down

$$g_n kT G_n^m[g_k] = g_n \sum_n W_{nk} g_k, \tag{10}$$

where W_{nk} is the average magnetic energy of interaction between the parallel n- and k-particle chains. This energy is

$$W_{nk} = -m^2 \int \left[\sum_{i=1}^{n} \sum_{j=1}^{k} \left(3\frac{\xi_{ij}^2}{r_{ij}^5} - \frac{1}{r_{ij}^3} \right) \right] dV. \tag{11}$$

Here r_{ij} is the distance between the ith particle in the n-particle chain and the jth particle in the k-particle chain, ξ_{ij} is the difference between the z coordinates of these particles in a coordinate system with the axis Oz aligned along the magnetic field (Fig. 2). Integration in Eq. (11) is over all positions of, say, the k-particle chain (the n-particle one is assumed to be fixed) taking into account that the chains cannot overlap.

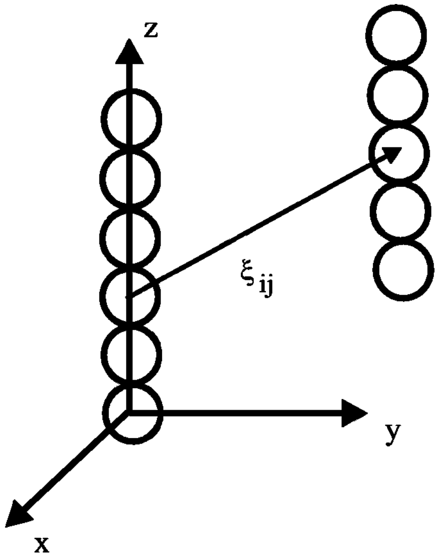

FIG. 2. Cartesian coordinate system, used for calculation of energy (12).

Let the origin of the Cartesian coordinate system, shown in Fig. 2, be in the center of the first particle in the first (n-particle) chain, and x, y, z be coordinates of the first particle in the second (k-particle) chain. Using the approximation of the chains as straight rods, we have

$$W_{nk} = -m^2 \sum_{i=1}^{n} \sum_{j=1}^{k} \int \left[3\frac{\xi_{ij}^2}{(\rho^2+\xi_{ij}^2)^{5/2}} - \frac{1}{(\rho^2+\xi_{ij}^2)^{3/2}} \right] dV, \tag{12}$$

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

De Gennes and Pincus have shown in Ref. [3] that the integral of type (12) from the potential of the dipole-dipole interaction depends on the shape of the volume of integration. The correct choice of this shape, as an infinitely long cylinder with axis aligned along the magnetic field, has been used in [13]. 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 macroscopical magnetic field in the place where two interacting particles are situated.

We have to take into account in integral (12) that the chains cannot interpenetrate. Because of a too complex surface of the chains, the exact form of the excluded volume for these chains is too cumbersome. To get reasonable estimates we present this excluded volume in the same form as for two spherocylinders with identical radius a and the lengths of the cylindrical part equaling $2a(n-1)$ 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 axes of the chains is significantly more than $2a$, that is typical for the "gas" and "liquid" states.

Using this approximation we can rewrite the integral in Eq. (12) as

$$\int \left[3\frac{\xi_{ij}^2}{(\rho^2+\xi_{ij}^2)^{5/2}}-\frac{1}{(\rho^2+\xi_{ij}^2)^{3/2}}\right]dV$$

$$=2\pi\left[\int_{2a}^{\infty}\rho d\rho\left(\int_{-\infty}^{\infty}\left(3\frac{\xi^2}{(\rho^2+\xi^2)^{5/2}}-\frac{1}{(\rho^2+\xi^2)^{3/2}}\right)d\xi\right)+S(n-1+j-i)+S(k-1+i-j)\right], \tag{13}$$

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 inner and this is to be calculated first. The integral over ρ is outer and to be calculated second. The order of integration is of principle importance here.

One can show that the first integral in square brackets of Eq. (13) is equal to zero. The function $S(x)$ can be presented as

$$S(x)=\frac{1}{2}\int_0^1\frac{\sqrt{1-y}+x}{(1+x^2+2x\sqrt{1-y})^{3/2}}dy$$
$$=K(x,s_2)-K(x,s_1), \tag{14}$$

where

$$K(x,s)=\frac{1}{4x^3}\left[\frac{1}{3}s^{3/2}-2s^{1/2}+(x^4-1)s^{-1/2}\right],$$

$$s_1=1+x^2, \quad s_2=(1+x)^2.$$

After transformations (12)–(14) we have

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

$$W_{nk}=-kT\gamma(2a)^3 2\pi\sum_{i=1}^{n}\sum_{j=1}^{k}[S(n-1+j-i)+S(k-1+i-j)]. \tag{15}$$

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

If 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

$$F^{st}=\frac{1}{2}kT\sum_n g_n G_n^{st}=\frac{1}{2}kT\sum_{nk} g_n g_k V_{nk}^{ex}, \tag{16}$$

where V_{nk}^{ex} is excluded volume for the n and k particle chains. As is well known the approximation of second virial coefficient for energy of a steric interaction is not sufficient to describe the condensation phase transition. The problem is how to generalize the equation (16) for the concentrated systems. This is one of the unsolved problems in the theory of dense systems of nonspherical particles, which is especially actual for statistical theory of liquid crystals. Simple, but successful approximations for F^{st} have been suggested by Parsons in Ref. [22] and used in theories [23,24] of nematiclike systems. According the to idea of [22], we may present the steric free energy in the following form:

$$F^{st}=\frac{1}{2}kT\sum_n g_n G_n^{st}=\frac{1}{2}kT\sum_{nk} g_n g_k V_{nk}^{ex} I(\varphi), \tag{17}$$

where $I(\varphi)$ is a function of the concentration φ only. 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 model again the chains as spherocylinders of radius $2a$ and lengths of the cylindrical parts $2a(n-1)$ and $2a(k-1)$, respectively. Using classical results of the Onsager theory [25], we have

$$V_{nk}^{ex}=6\left(n+k-\frac{2}{3}\right)v. \tag{18}$$

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 approximation gives

$$F^{st}=\frac{1}{2}kTg_1g_1v8\frac{1-\frac{3}{4}\varphi}{(1-\varphi)^2}. \tag{19}$$

At the same time for these spheres $V_{11}^{ex}=8v$. Comparing Eqs. (17), (18) and (19), one can get

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

and therefore

$$G_n^{st}=6kT\frac{1-\frac{3}{4}\varphi}{(1-\varphi)^2}v\sum_k\left(n+k-\frac{2}{3}\right)g_k. \tag{20}$$

Finally, combining Eqs. (1), (9), (10), (15), (17), and (20), we obtain

$$F=kT\sum_n\left(g_n\ln\frac{g_n}{e}+g_nf_n+\frac{1}{2}g_n\sum_k g_k\Phi_{nk}\right),\tag{21}$$

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

V. THE SIZE DISTRIBUTION FUNCTION

Let us find now the distribution function g_n. Minimizing F in Eq. (21), taking into account condition (2) and Eq. (8), we get

$$g_n=\frac{1}{v}\exp\left(-f_n-\sum_k g_k\Phi_{nk}-\lambda n\right)=\frac{1}{v}X^n\exp\left(-\varepsilon_*-\sum_k g_k\Phi_{nk}\right),\tag{22}$$

$$X=\exp(\alpha+\varepsilon_*-\lambda),\quad \varepsilon_*=\ln J(\gamma),$$

where J is the same as in Eqs. (6) and (7). Parameter λ here is a Lagrange multiplier. Its physical meaning is chemical potential of particles.

To determine λ (or, that is the same, parameter X), we are to substitute Eq. (22) into Eq. (2). As a result we come to a nonlinear equation of integral type for g_n. This equation can be solved only by using an iteration procedure. To organize this procedure we take into account that, as simple considerations show, the mean energy of interaction between particles in different chains is weaker than the energy $kT2\gamma$ of interaction between the neighbor particles in one chain. Indeed, the neighbor particles in one chain are situated in places close to positions of the maximum of absolute magnitude of energy of their dipole-dipole interaction. Particles from different chains cannot be situated in these occupied positions (otherwise they must be considered as belonging to one chain). Then, the different chains are in a certain mean distance from each other. Thus, interaction between particles, belonging to different chains, really is weaker then the interaction between contacting particles in the chain. Therefore, in the first approximation, we may neglect influence of the interaction between chains on the distribution function g_n and rewrite Eq. (22) as

$$g_{0n}=X_0^n\exp(-\varepsilon_*)=X_0^nJ(\gamma)^{-1},\tag{23}$$

where the index 0 means that we neglect any interactions between the chains (zero iteration for determination g_n).

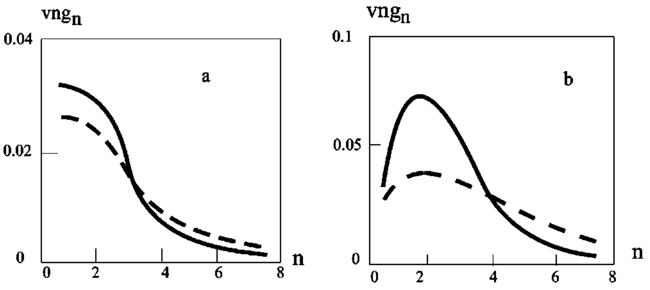

FIG. 3. Volume concentration vng_n of the n-particle chains for $\gamma=3.5$ and $\varphi=0.05$ (a) and 0.1 (b). Solid lines: g_n is calculated in approximation (25); dashed lines: in approximations (23) and (25) of the noninteracting chains.

Substituting Eq. (23) into Eq. (2) after calculations, described in detail in Refs. [2], we get

$$X_0=\frac{1+2\varphi\exp(\varepsilon_*)-\sqrt{1+4\varphi\exp(\varepsilon_*)}}{2\varphi\exp(\varepsilon_*)}=\frac{1+2\varphi J(\gamma)-\sqrt{1+4\varphi J(\gamma)}}{2\varphi J(\gamma)}.\tag{24}$$

The combination of Eqs. (23) and (24) gives us the size distribution function in the approximation of the noninteracting chains placed into an infinitely strong field.

Using now the function g_{0n} in the right side of Eq. (22), we come to the following approximate expression for the distribution function with account of effects of interchain interaction

$$g_{1n}=\frac{1}{v}X_1^n\exp\left(-\varepsilon_*-\sum_k g_{0k}\Phi_{nk}\right).\tag{25}$$

Using here Eqs. (23) and (24) and substituting Eq. (25) with Eq. (2), we come to the transcendent equation for X_1. Solving this numerically, we find distribution function g_{1n} corresponding to the first step of the iteration procedure. This procedure can be continued.

Some results of calculations of the functions g_{on} and g_{1n} are shown in Figs. 3 and 4. The physical meaning of the term vg_nn is volume concentration of the n-particle chains in the system. When parameters φ and γ are not very small, this concentration, as a function of n, demonstrates maximum. These maxima appear also in models [20] of the polymerlike chains without field and in a simple model [2] where the chains are treated as straight rodlike aggregates. As follows from comparison of the plots, corresponding g_{0n} and to g_{1n},

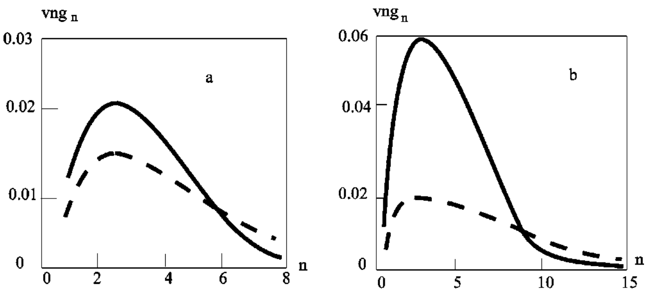

FIG. 4. The same as in Fig. 3 for $\gamma=4.5$.

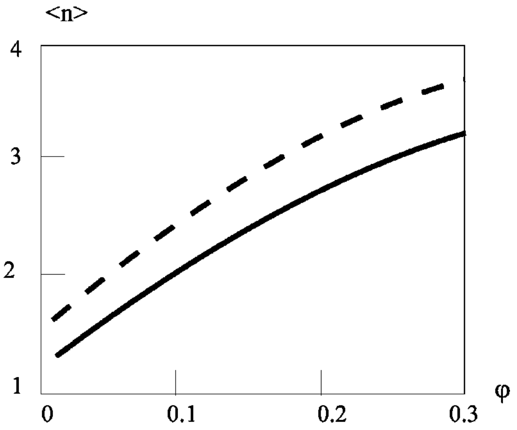

FIG. 5. The mean number $\langle n\rangle$ of the particles in the chains vs volume concentration φ for $\gamma=3.5$. Solid line corresponds to approximation (25) and dashed line to Eqs. (23) and (24).

the interaction between the chains leads to a more sharp maximum of the volume concentration and decreases the number of the long chains.

The mean number of the particles in the chains (including single particles) is

$$\langle n\rangle=\frac{\varphi}{v\sum_{n=1}^{\infty}g_n}. \tag{26}$$

In the model of noninteracting chains [approximations (23) and (24) for g_n] calculations give

$$\langle n\rangle=\varphi J(\gamma)\frac{1-X_0}{X_0}. \tag{27}$$

When the dipole-dipole interaction between particles is strong ($\varphi J\gg 1$) Eq. (27) can be transformed to the following form:

$$\langle n\rangle\approx\varphi^{1/2}J^{1/2}.$$

This estimate in logarithmic approximation coincides with scaling approximation, discussed in Ref. [20]. In the model of interacting chains [approximation (25)] the mean number $\langle n\rangle$ can be calculated only numerically.

Calculations of $\langle n\rangle$ carried out in approximations (27) (noninteracting chains) and Eqs. (25) and (26) (interacting chains) are shown in Figs. 5 and 6 for two different magnitudes of γ. The results demonstrate that the interaction between the chains decreases $\langle n\rangle$ as compared with those in the model of the noninteracting chains. It appears because of decreasing of the total number of the particles united into the long chains.

The fact that the interaction between the chains decreases their mean length was noted also in [20] for the case of zero magnetic field. Qualitatively this corresponds to observations in numerical experiments [16] where chains take place only in dilute enough systems, whereas in a highly concentrated ensemble of ferroparticles separate linear clusters are absent.

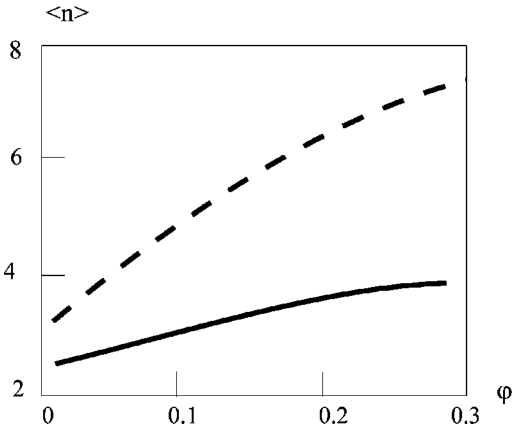

FIG. 6. The same as in Fig. 5 for $\gamma=4.5$.

The fact that the qualitatively similar results were obtained in different models for different limit situations (zero and infinitely strong magnetic fields) shows general conformity to natural laws with respect to influence of the interaction between the chains on their characteristic size.

VI. CONCLUSION

Influence of chain-chain interaction on the size distribution of these chains in ferrofluids placed into an infinitely strong magnetic field is studied. We show that for high enough total volume concentration of the particles and energy of their magnetic interaction, the function of distribution for the chains over the number of the particles inside them is a nonmonotonic function with maximum corresponding to certain n. The chain-chain interaction increases this maximum and makes the pick more narrow as compared with the results in the model of the noninteracting chains. Therefore, the number of free particles as well as the particles united into long chains decreases due to the interaction between the chains. As a result the mean number of the particles in the chains decreases due to this interaction.

It should be noted that since the functional F of free energy is nonlinear with respect to distribution function g_n, generally speaking, this can have several extremums [Eqs. (2) and (22) can have several solutions]. However, known mathematical methods do not allow us to investigate analytically the nonlinear functional F in the general case. At the same time, when concentration φ of particles is low enough, and the chain-chain interaction is weaker than interaction between neighbor particles in one chain [parameter ε_* in Eq. (25) is significantly more than $\Sigma_k g_{0k}\Phi_{nk}$], the iteration procedure used is justified. For ferrofluids with a high density of particles, the system (2) and (22) can be studied only numerically. This analysis is worth a separate work.

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