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Initial Magnetic Susceptibility of Ferrocolloids: The Influence of Chain Aggregates

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Abstract—The behavior of a system of noninteracting chain aggregates of ferroparticles suspended in a liquid matrix and subjected to a weak uniform permanent magnetic field was studied based on the free energy functional of a monodisperse low-concentration magnetic colloid. The orientational response of a flexible chain to a weak external field showed that the model of rigid rods is applicable only for short chains (doublets and triplets) of large ferroparticles characterized by a strong magnetodipole interaction. The calculated values of the initial magnetic susceptibility of aggregated ferrofluid agree well with the computer simulation data.

1. INTRODUCTION

Ferrocolloids (ferrofluids, magnetic fluids) are the stable suspensions of the particles of ferro- or ferrimagnetic materials (iron, cobalt, and nickel oxides) in liquids. The characteristic diameter of magnetic cores is equal to about 10 nm, i.e., it is smaller than the size of magnetic domains. Therefore, each ferroparticle possesses magnetic moment **m** whose value is proportional to the volume of the magnetic core of a particle and the saturation magnetization of corresponding bulk magnetic material. The external magnetic field produces an orienting effect on the particle magnetic moments to thereby impart to ferrofluids the ability to interact with the magnetic field with the conservation of the features of liquid state. On the one hand, such a unique combination leads to many unexpected physicochemical effects and, on the other hand, allows to refer the magnetic fluids to the class of substances with controllable properties, thus predetermining their extensive application in modern technologies.

The computer simulation of ferrofluids and polar liquids by the Monte Carlo method and molecular dynamics performed from the beginning of the 1990s [1–11] demonstrated that the internal microstructure of such systems seems to be much more complex compared to the uniform colloidal suspension of single magnetic particles. At low particle concentrations and their intense magnetic interaction, the developed structure of chain aggregates is formed in a system [3–11], whereas, at high particle concentrations, the spontaneous formation of ferroelectric structure was observed [1, 2]. The presence of attractive central interaction between particles (the Stockmayer fluid) leads to the condensation phase transition [9].

A large volume of experimental data is available that demonstrates not only the existence of chain aggregates in ferrofluids, but also their significant influence on optical [12–15], rheological [16–18], and other physicochemical [19–22] properties of ferrofluids. The condensation of ferroparticles known as a phase separation was also repeatedly observed in experiments [23, 24]. Note that there are no direct experimental evidences of the spontaneous magnetization of magnetic colloids.

Because any types of microstructural formations in polar liquids and magnetic colloids seem to be very significant for the physics of liquid state due to their substantial effect on the macroscopic properties of these systems, they are extensively studied theoretically. Specific features of magnetic fluids are determined by dipole-dipole interaction U_d of magnetic moments of ferroparticles

$$U_d(ij) = -\left[3\frac{(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} - \frac{(\mathbf{m}_i \cdot \mathbf{r}_j)}{r_{ij}^3}\right], \qquad (1)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$; $\mathbf{r}_i$ and $\mathbf{r}_j$ are the vector-radii of ith and jth particles, respectively; As is seen from Eq. (1), $U_d\,(ij)$ depends not only on distance r_{ij} between ferroparticles, but also on the mutual orientation of their magnetic moments $\mathbf{m}_i$ and $\mathbf{m}_j$, and can correspond both to attraction and repulsion. The most energy favorable position of the particle pair is their contact (doublet) with the "head-to-tail" orientation of magnetic moments. Therefore, the most typical (for ferrofluids) are the aggregates in the form of flexible chains composed of ferroparticles (Fig. 1). Naturally, such microstructural formations can exist only in ferrofluids with sufficiently large particles intensely interacting with each other. The parameter of magnetodipole interaction $\lambda = m^2/d^3kT$ is traditionally used as a measure of such intensity. This parameter has the meaning of the ratio between the characteristic interaction energy of the magnetic moments of two particles upon their contact, m^2/d^3, and thermal energy kT (d is the diameter of ferroparticle with the steric shell). For real ferrofluids where most of the particles has the sizes of ≈10 nm, the average value of parameter λ does not exceed unity. However, for the

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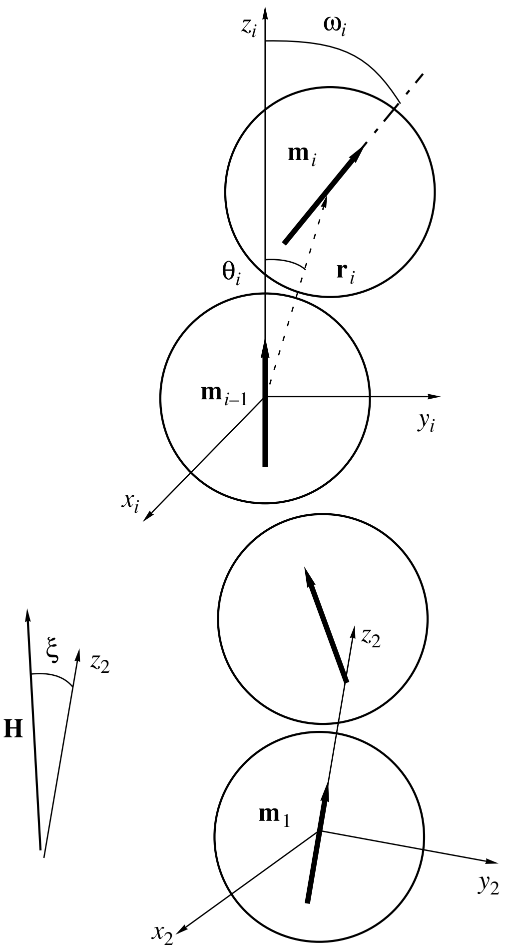

Fig. 1. Coordinate system employed for calculating configuration integral of the chain.

particles of coarse fractions with sizes of ≈15–18 nm, which are always present in real ferrofluids, this parameter can be as high as $\lambda \approx 3$–5 nm.

Two main theoretical approaches to the analysis of the properties of chain structures are developed at present. The first approach is based on the principles of dynamic equilibrium between chains of different lengths [25]; in this case, the attachment/detachment process of single particles is treated as a chemical reaction. In other approach, which is equivalent to the first one from the standpoint of statistical mechanics, the condition of free energy minimum of a system as a functional of chain distribution density over the number of constituting particles is used [26–32]. The formation of chain aggregates in the monodisperse systems of magnetic particles was studied in these works. However, there are studies where the polydispersity of real ferrofluids was taken into account [33–35].

Only the limiting cases of the absence of field infinitely strong external field were considered in theoretical works [28–35]. The mathematical aspect of a problem is slightly simplified in these cases; hence, one can succeed in deriving the explicit expression for chain length distribution. However, since the main interest to ferrofluids is due to their ability to interact with the external magnetic field, the problem of the influence of this field on chain aggregates becomes fundamentally important. There is no solution to the problem of the effect of the external field strength on the aggregate properties. The attempt to solve this problem was undertaken only in [26, 27], but for the chains in the form of rigid rods. The abandonment of the account of intrachain fluctuations leads to the obvious overestimation of system response to the external magnetic field. Therefore, the solution derived in [26, 27] can be regarded only as a qualitative estimation that is approximately valid for the particles characterized by a high value of parameter λ.

This work is devoted to the analysis of the orientational response of a system of chain aggregates to weak uniform permanent magnetic field. Assumptions that are traditional for chain models are employed: the interparticle interaction inside chains is taken into account only for the nearest neighbors; for low-concentration ferrofluids, the interaction between the chains is disregarded. This model takes advantage of the condition of minimum of the free energy functional (Section 2); the matrix method of coordinate system rotation is employed for calculating the configuration integral of a chain. Using this technique, we studied in Section 3 the orientational response of a single chain to the weak external field and introduced the notion of correlation coefficient for the directions of the magnetic moments of two neighbor ferroparticles. The dependence of this coefficient on the intensity of interparticle dipole–dipole interactions, as well as on the admissible orientational and spatial intrachain fluctuations, is studied in Section 4. An exact (within the framework of assumed approximations) expression for the initial magnetic susceptibility of the ideal gas of the chains of ferroparticles suspended in a liquid matrix is derived in Section 5. Main conclusions are formulated in final Section 6.

2. FREE ENERGY FUNCTIONAL

The traditional approach to the description of chain aggregates in ferrofluids [26–35] is based on Frenkel's theory of heterophase fluctuations. The monodisperse ferrofluid is considered as a mixture of chain aggregates of various lengths, where each particle is a single structural element possessing intrinsic translational and orientational degrees of freedom. For low concentrated systems, the dipole–dipole interaction is accounted only for the particles belonging to one chain. Thus, the density of free energy F is represented as a sum of the free energy of the mixture of the ideal gases of chains with various lengths suspended in a liquid matrix and free energies of single chains

$$F = kT\sum_{n=1}^{\infty} g_n(H)\left(\ln\frac{g_n(H)v}{e} - \ln Q_n(H)\right). \qquad (2)$$

Here, g_n and Q_n are the concentration and configuration integral of chains composed of n particles, respectively, and $v = \pi d^3/6$ is the volume of a ferroparticle with the steric shell. The chain particle number distribution g_n is determined from the minimum condition of functional $F[g_n]$ (2) when accounting for the material balance in a system

$$\sum_{n=1}^{\infty} n g_n(H) = \frac{\rho}{v}, \tag{3}$$

where ρ is the volume density of dispersed phase in a ferrofluid.

In functional (2), the specificity of chain microinclusions is determined by the form of configuration integral Q_n, which, with allowance made for the interactions only between the nearest neighbors in a chain, has the following form:

$$Q_n(H) = \frac{1}{v^{n-1}} \int \prod_{i=1}^{n} d\tau_i \exp\left(-\frac{U_s + U_d + U_m}{kT}\right),$$

$$U_s = \sum_{i=1}^{n-1} U_s(i\ i+1), \quad U_d = \sum_{i=1}^{n-1} U_d(i\ i+1), \tag{4}$$

$$U_m = \sum_{i=1}^{n} U_m(i) = -\sum_{i=1}^{n} (\mathbf{m}_i \cdot \mathbf{H}),$$

where $d\tau_i$ is the element of phase volume in the space of positions and orientations of ith particle in a chain; U_s and U_d are the potential energies of central and dipole–dipole pair interparticle interactions, respectively; and U_m accounts for the interaction between the particles and external uniform permanent magnetic field $\mathbf{H}$. The central symmetric part of interaction energy $U_s(r_{ij})$ includes the sterical repulsion, van der Waals attraction, and the electrostatic repulsion of electrical double layers (for electrostatically stabilized ferrofluids). In order to ignore the effects of demagnetization, the volume of ferrocolloid is assumed to be in the form of ellipsoid of revolution strongly stretched along the direction of the field. In this case, the value of local internal field acting on a single magnetic particle coincides with the external field.

Therefore, we confined ourselves only to the consideration of microinclusions in the form of chain aggregates; the coordinate system, where the orientation and position of each ith particle is determined with respect to the preceding i – 1th particle in a chain, is the most convenient (Fig. 1). The origin of each such ith coordinate system is located in the center of i – 1th particle so that the Oz_i axis is directed along i – 1th magnetic moment. Correspondingly (Fig. 1), the direction of the magnetic moment of each i – 1th particle in ith coordinate system is determined by the unit vector

$$\mathbf{n} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

In each ith coordinate system, the radius vector and magnetic moment of i – 1th particle are set by standard rotation matrices $\mathbf{R}_i$ and $\mathbf{T}_i$ [25]

$$\mathbf{r}_{i-1\,i} = r_i \mathbf{R}_i \mathbf{n}, \quad \mathbf{m}_i = m \mathbf{T}_i \mathbf{n},$$

$$\mathbf{R}_i = \begin{pmatrix} \cos\theta_i \cos\varphi_i & -\sin\varphi_i & \sin\theta_i \cos\varphi_i \\ \cos\theta_i \sin\varphi_i & \cos\varphi_i & \sin\theta_i \sin\varphi_i \\ -\sin\theta_i & 0 & \cos\theta_i \end{pmatrix}, \tag{5}$$

$$\mathbf{T}_i = \begin{pmatrix} \cos\omega_i \cos\zeta_i & -\sin\zeta_i & \sin\omega_i \cos\zeta_i \\ \cos\omega_i \sin\zeta_i & \cos\zeta_i & \sin\omega_i \sin\zeta_i \\ -\sin\omega_i & 0 & \cos\omega_i \end{pmatrix}.$$

In expressions (5), vector Ω_i (ω_i, ζ_i) determines the direction of magnetic moment of ith particle ($\mathbf{m}_i = m\Omega_i$) and vector $\mathbf{r}_i$ (r_i, θ_i, φ_i) connects the centers of i – 1th and ith particles in a chain (i = 2, …, n); i.e., has the same meaning as vector $\mathbf{r}_{i-1\,i}$ (5). However, since vector $\mathbf{r}_i$ starts from the center of reference of ith coordinate system, its direction and length depend only on the position of ith particle. In order to emphasize such feature of this particle, we used here the new designation for the radius vector.

The orientation of the entire chain with respect to the external magnetic field is set by angle ξ between the directions of field $\mathbf{H}$ and magnetic moment $\mathbf{m}_1$ of the first particle (Fig. 1) so that the field vector has the coordinates

$$\mathbf{H} = H \begin{pmatrix} \sin\xi \\ 0 \\ \cos\xi \end{pmatrix}. \tag{6}$$

Because configuration integral (4) includes the averaging over all possible directions of chains in a system bulk, it is evident that the variation of angle within $0 \le \xi \le \pi$ range is equivalent to the account of all such orientations. In other words, not all possible directions of particles are accounted for, but the rotation of magnetic field is performed around a single randomly chosen chain. In addition, the averaging over corresponding polar angle that does not contribute to the configuration integral was immediately performed in expression (6). This follows from the fact that magnetic interaction $U_m(1)$ depends only on the cosine of angle ξ. In order to determine magnetic interaction potential $U_m(i)$ of all other particles in the chain and connect ith magnetic moment $\mathbf{m}_i$ with the vector of magnetic field $\mathbf{H}$, it is necessary to consecutively rotate and shift the coordinate system from i – 1th particle to the first one

$$\mathbf{r}_{i-1\,i} = r_i \mathbf{T}_2 \ldots \mathbf{T}_{i-1} \mathbf{R}_i \mathbf{n}, \quad \mathbf{m}_i = m \mathbf{T}_2 \ldots \mathbf{T}_i \mathbf{n}. \tag{7}$$

Unlike expressions (5), these relations determine the coordinates and orientations of ith particle with respect to the first particle (Fig. 1) and the field direction.

As a result, configuration integral (4) acquires the following form:

$$Q_n(H) = \frac{1}{V^{n-1}}$$

$$\times\int_0^{\pi}\frac{\sin\xi d\xi}{2}\int\prod_{i=2}^{n}d\mathbf{r}_i\int\prod_{i=2}^{n}d\Omega_i\exp\left(-\frac{U_s+U_d+U_m}{kT}\right), \quad (8)$$

$$d\Omega_i = (4\pi)^{-1}\sin\omega_i d\omega_i d\zeta_i, \quad d\mathbf{r}_i = r_i^2 dr_i\sin\theta_i d\theta_i d\varphi_i,$$

where the integration with respect to variables $\mathbf{\Omega}_i$ and $\mathbf{r}_i$ corresponds to the averaging over all fluctuations of form and moment orientations inside the chain with the account of the normalization in the space of orientations; the integration with respect to ξ denotes the normalized averaging over all possible directions of flexible chain with respect to external field. This representation of the configuration integral proposed for the first time in [25] seems to be very convenient, because when writing each potential of dipole–dipole interaction (1) between the i and $i-1$ nearest neighbors in the chain, the orientation of $i-1$th moment is determined by unit vector $\mathbf{n}$. On the other hand, magnetic part U_m of potential energy becomes more complex and acquires the form

$$-U_m/kT = \alpha\sum_{i=1}^{n}Z_i, \quad (9)$$

where Langevin multiplier $\alpha = mH/kT$ corresponds to the ratio of the characteristic energy of interaction between the magnetic moment and the external field to thermal energy, and the Z_i values are equal to the cosines of corresponding angles. For their successive determination, one should use recurrent relations derived in the method of matrix rotation

$$Z_i = X_{i-1}\sin\omega_i\cos\zeta_i + Y_{i-1}\sin\omega_i\sin\zeta_i + Z_{i-1}\cos\omega_i,$$
$$X_i = X_{i-1}\cos\omega_i\cos\zeta_i + Y_{i-1}\cos\omega_i\sin\zeta_i - Z_{i-1}\sin\omega_i,$$
$$Y_i = -X_{i-1}\sin\zeta_i + Y_{i-1}\cos\zeta_i, \quad i \ge 2, \quad (10)$$
$$X_1 = \sin\xi, \quad Y_1 = 0, \quad Z_1 = \cos\xi,$$
$$X_i^2 + Y_i^2 + Z_i^2 = 1.$$

Configuration integral (8) is substantially simplified when the external filed is absent, because the successive integration with respect to the degrees of freedom of all particles in a chain, beginning with the last particle, and the rotation of coordinate system lead to the same $n-1$th multiplier

$$Q_n(0) = q_0^{n-1},$$

$$q_0 = \int\frac{d\mathbf{r}_2}{V}\int d\Omega_2\exp\left[-\frac{U_d(12)+U_s(12)}{kT}\right], \quad (11)$$

$$\mathbf{m}_1 = m\mathbf{n}.$$

This feature of the factorization of the configuration integral is valid also in the case of infinitely strong magnetic field, because the orientational degrees of freedom become degenerated

$$Q_n(\infty) = q_\infty^{n-1},$$

$$q_\infty = \int\frac{d\mathbf{r}_2}{V}\exp\left[-\frac{U_d(12)+U_s(12)}{kT}\right], \quad (12)$$

$$\mathbf{m}_1 = \mathbf{m}_2 = m\mathbf{n}.$$

In the magnetic field of arbitrary strength, such a factorization is absent, since the magnetic moments of all particles in the chain become correlated due to their interaction with the external field. That is why the structure of chain aggregates in an arbitrary field has not been so far studied.

3. CONFIGURATION INTEGRAL OF A CHAIN IN A WEAK MAGNETIC FIELD

When studying the magnetic properties of ferrofluids, the response of a system to infinitely weak field (initial static magnetic susceptibility) is of the most interest. In this case

$$\exp(-U_m/kT) \approx 1 + \frac{\alpha^2}{2}\left(\sum_{i=1}^{n}Z_i\right)^2$$
$$= 1 + \frac{\alpha^2}{2}\sum_{i=1}^{n}Z_i^2 + \alpha^2\sum_{k<j=1}^{n}Z_kZ_j, \quad (13)$$

where linear (with respect to α) term vanishes because of a system symmetry. Further transformations are based on two facts. First, all Z_i values are independent of polar angles φ_i. Second, each polar angle φ_i is present in integrand exponent (8) only once in corresponding potential U_d $(i-1i)$. The use of common transformation

$$\int_0^{2\pi}f(A\cos\varphi + B\sin\varphi)d\varphi = \int_0^{2\pi}f(\sqrt{A^2+B^2}\cos\varphi)d\varphi$$

allows us to reduce all potentials of interparticle dipole–dipole interaction to the form (each in its own coordinate system)

$$-\frac{U_d(i-1\ i)}{kT} = \frac{\lambda}{r_i^3}$$
$$\times[\cos\omega_i(3\cos^2\theta_i - 1) + 3\sin\omega_i\sin\theta_i\cos\theta_i\cos\varphi_i]. \quad (14)$$

Then, all integrand exponents with potentials of dipole–dipole interaction (8) cease to depend on angles ζ_i. The dependence of these angles remains only in Z_i (13). These values depend also on angle ξ; however, the dependence on ξ and ζ_i is such that makes it possible to integrate multiplier (13) separately with respect to all angles ζ_i and ξ. Let us now consider all terms entering into this factor separately

$$\int_0^\pi \frac{\sin\xi d\xi}{2} Z_1^2 = \int_0^\pi \frac{\sin\xi d\xi}{2}\cos^2\xi = \frac{1}{3},$$

$$\int_0^\pi \frac{\sin\xi d\xi}{2}\int_0^{2\pi}\frac{d\zeta_2}{2\pi}Z_2^2 = \int_0^\pi \frac{\sin\xi d\xi}{4}$$

$$\times[\sin^2\omega_2 + (3\cos^2\omega_2 - 1)Z_1^2] = \frac{1}{3},$$

$$\int_0^\pi \frac{\sin\xi d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{j}\frac{d\zeta_i}{2\pi}Z_j^2 = \int_0^\pi \frac{\sin\xi d\xi}{4}\int_0^{2\pi}\prod_{i=2}^{j-1}\frac{d\zeta_i}{2\pi}$$

$$\times[\sin^2\omega_j + (3\cos^2\omega_j - 1)Z_{j-1}^2] = \frac{1}{3}.$$

In other words, the average of all Z_i^2 becomes identical

$$\int_0^\pi \frac{\sin\xi d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{n}\frac{d\zeta_i}{2\pi}\sum_{i=1}^{n}Z_i^2 = \frac{n}{3}.$$

Let us consider the averaging of cross terms Z_kZ_j, $k < j$ in expression (13)

$$\int_0^\pi \frac{\sin\xi d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{j}\frac{d\zeta_i}{2\pi}Z_kZ_j$$

$$= \int_0^\pi \frac{\sin\xi d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{j-1}\frac{d\zeta_i}{2\pi}Z_kZ_{j-1}\cos\omega_j$$

$$= \int_0^\pi \frac{\sin\xi d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{k}\frac{d\zeta_i}{2\pi}Z_k^2\prod_{m=k+1}^{j}\cos\omega_m = \frac{1}{3}\prod_{m=k+1}^{j}\cos\omega_m.$$

Thus, for weak fields, the averaging of expression (13) for the chain composed of n particles over all angles ζ_i and ξ gives

$$\int_0^\pi \frac{\sin\xi d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{n}\frac{d\zeta_i}{2\pi}\exp(-U_m/kT)$$
$$\approx 1 + \frac{\alpha^2}{6}\left(n + 2\sum_{k<j=1}^{n}\prod_{m=k+1}^{j}\cos\omega_m\right). \tag{15}$$

The use of this expression in configuration integral (8) permits us to transform it to the form

$$Q_n(H \longrightarrow 0) = \frac{1}{V^{n-1}}$$
$$\times\int\prod_{i=2}^{n}d\mathbf{r}_i\int_0^\pi\frac{\sin\omega_i d\omega_i}{2}\exp\left(-\frac{U_s + U_d}{kT}\right) \tag{16}$$
$$\times\left[1 + \frac{\alpha^2}{6}\left(n + 2\sum_{k<j=1}^{n}\prod_{m=k+1}^{j}\cos\omega_m\right)\right],$$

where all dipole–dipole potentials are determined by formula (14). Note that expression (16) can be factored again, because it represents the combinatorial sum of the terms composed of independent factors

$$Q_n(H \longrightarrow 0) = q_0^{n-1}\left[1 + \frac{\alpha^2}{6}\left(n + 2\sum_{k<j=1}^{n}K^{j-k}\right)\right]$$
$$= q_0^{n-1}\left\{1 + \frac{\alpha^2}{6}\left[n + 2\frac{K}{(1-K)^2}(n - 1 + K^n - nK)\right]\right\}. \tag{17}$$

Here, we introduced designation K for the correlation coefficient between the directions of the magnetic moments of neighbor particles in the chain (the average value of the projection of one moment on the other moment)

$$K = q_0^{-1}\int\frac{d\mathbf{r}_2}{V}\int d\Omega_2\cos\omega_2\exp\left[-\frac{U_d(12) + U_s(12)}{kT}\right]. \tag{18}$$

It is evident that the value

$$\langle m_n\rangle = \sqrt{n + 2\frac{K}{(1-K)^2}(n - 1 + K^n - nK)} \tag{19}$$

has the meaning of dimensionless root-mean-square magnetic moment of the chain composed of n particles. In the limiting case of rigid rodlike chain ($K = 1$),

$$\langle m_n\rangle = n, \quad Q_n(H \longrightarrow 0) = q_0^{n-1}\left(1 + \frac{\alpha^2 n^2}{6}\right), \tag{20}$$

that corresponded to the approximation (used in [26, 27]) of the ideal gas of the chains of various lengths whose magnetic moment $\mathbf{m}_n$ is equal to $\mathbf{m}_n = n\mathbf{m}$. Figure 2 shows the dependence of dimensionless root-mean-square magnetic moment of the chain, $\langle m_n\rangle/n$, related to the number of particles in the chain, on correlation coefficient K. It is seen that the chain can be considered as rigid and rodlike ($\langle m_n\rangle/n \approx 0.9$ and larger) only at sufficiently large values of correlation coefficient ($K \approx 0.9$ and larger). Moreover, short chains (doublets and triplets) become "rigid" before the long ones. This quite expected fact is associated with stronger bending fluctuations of long chains.

4. CORRELATION COEFFICIENT OF NEIGHBOR MAGNETIC MOMENTS IN THE CHAIN

As follows from definition (18), the correlation coefficient depends on the intensity of dipole–dipole interaction, the type of central part of interparticle interaction U_s, and the admissible spatial and orientational fluctuations for each pair of neighbor particles (i.e., on the integration domain in expressions (11) and (18)). Fluctuation contribution depends actually on the calculation procedure for configuration integral q_0 of doublet (11) in the absence of external filed. The asymptotic method of integral estimation (the saddle point approx-

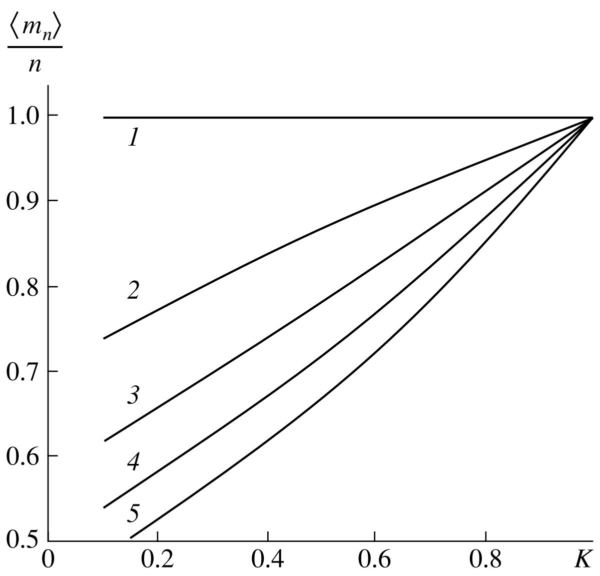

Fig. 2. Dependences of dimensionless root-mean-square magnetic moment of the chain, $\langle m_n \rangle / n$, related to the number of particles in the chain on the correlation coefficient K for chains consisting of different number of particles n: (*1*) 1, (*2*) 2, (*3*) 3, (*4*) 4, and (*5*) 5.

imation) is most frequently used. For central potential U_s corresponding to the interaction U_{HS} between hard spheres with a diameter of d, the following approximation expressions:

$$q_0 \approx \exp(2\lambda)/(3\lambda^3), \quad K \approx 1 - 2/\lambda, \quad \lambda \gg 1 \tag{21}$$

were derived for q_0 and K [25]. More exact relations were derived in [32] within the framework of similar approach

$$q_0 = \frac{\exp(2\lambda)}{3\lambda^3}$$
$$\times\left(1 + \frac{8}{3\lambda} + \frac{23}{3\lambda^2} + \frac{229}{9\lambda^3} + \frac{5263}{54\lambda^4} + \frac{11\,536}{27\lambda^5} + \frac{57\,427}{27\lambda^6}\right),$$
$$K = 1 - \frac{2}{\lambda} - \frac{2}{\lambda^2} - \frac{20}{3\lambda^3} - \frac{266}{9\lambda^4} - \frac{4241}{27\lambda^5} - \frac{77\,669}{81\lambda^6}, \tag{22}$$
$$\lambda \gg 1.$$

Note that, even for unrealistic large (for ferrofluids) values $\lambda = 10$, expressions (21) and (22) yield correlation coefficient $K \approx 0.8$. This means that such an approach admits rather high orientational mobility of magnetic moments inside dimers. In fact, this result follows from the calculation scheme of configuration integral of dimers (21) and (22), according to which unfavorable (in advance) configurations corresponding to angles $0 \le \theta_2 \le \pi/2$ and $0 \le \omega_2 \le \pi$ are taken into account. In addition, the gaps with a thickness of $\delta \approx d/6\lambda$ between the particles are admitted. It follows from the comparison of relations (21) and (22) that smaller values of correlation coefficient K correspond to large q_0 values.

The model of “soft” spheres was employed in the computer simulation of the magnetic properties of aggregated ferrofluids by the molecular dynamics method [10, 11]: central potential U_s had the form of the repulsive term of the Lennard-Jones potential

$$-U_s(r)/kT = [1 - 2(d/r)^6]^2, \quad 0 < r < 2^{1/6}d, \tag{23}$$

where r is the distance between the centers of neighbor ferroparticles. Correlation coefficient K (18) for this potential appeared to be rather sensitive to the choice of the domain of integration with respect to angles θ_2 and ω_2. To demonstrate this effect, we consider four domains of integration which can be realized when calculating q_0 and K:

(1) $0 \le \omega_2 \le \pi$, $0 \le \theta_2 \le \pi/2$, $0 < r_2 < 2^{1/6}d$ that corresponds to all possible orientations of the second magnetic moment with respect to the first moment, the position of the second particle in the upper hemisphere for the first particle (Fig. 1), and their soft contact;

(2) $0 \le \omega_2 \le \pi/2$, $0 \le \theta_2 \le \pi/2$, $0 < r_2 < 2^{1/6}d$. This case differs from the previous one by that the orientation of the second magnetic moment is admitted only in the upper hemisphere in the space of orientations of the first moment so that $\cos\omega_2 \ge 0$;

(3) $0 \le \omega_2 \le \pi/2$, $0 \le \theta_2 \le \arccos(1/\sqrt{3})$, $0 < r_2 < 2^{1/6}d$; here, the additional constraint on the deviation of radius vector $\mathbf{r}_2$ from the Oz_2 axis was used: $3\cos^2\omega_2 - 1 \ge 0$ (see expression (14));

(4) the domain of connected (by definition [10, 11]) particles: the particles are considered as connected into the chain, if the absolute value of the energy of their dipole–dipole interaction is no less than 70% of maximal energy of contact interaction equal $2\lambda kT$ or $U_d \le -1.4\lambda kT$.

Explicit expressions for the q_0 and K values in all the cases can be derived from definitions (11) and (18) upon the substitution of potentials (14) and (23) and the arrangement of corresponding integration limits. The calculation results are shown in Figs. 3 and 4. Similar, as for relations (21) and (22), correlation is observed: smaller K values correspond to large q_0 values. This seems quite evident, because the passage from case (1) to case (4) is associated with a decrease in the domain of integration in definitions (11) and (18), thus decreasing the value of configuration integral of doublet q_0 (Fig. 3, curves *1–4*). On the other hand, constraints on admissible orientational fluctuations inside the doublet become stronger; hence, the correlation of neighbor magnetic moments increases (Fig. 4, curves *1–4*). For region 4, the doublet can be considered as a rigid rod, the correlation coefficient is actually constant ($K \approx 0.91$). However, the q_0 values turned out to be very low. In other words, the number of such rigid rodlike chains is small and they are short.

5. INITIAL SUSCEPTIBILITY OF FERROFLUID WITH CHAIN AGGREGATES

The response of noninteracting chains to the uniform permanent external field (system magnetization M) can generally be calculated from the functional of free energy (2) and (3)

$$M(H) = kT\sum_{n=1}^{\infty} g_n(H)\frac{\partial \ln Q_n(H)}{\partial H}. \tag{24}$$

Using the results obtained above, for the initial susceptibility χ of a system of noninteracting chains, we find

$$\begin{aligned}\chi &= \frac{2\lambda}{\pi}\sum_{n=1}^{\infty} g_n(0)\left[n + 2\frac{K}{(1-K)^2}(n-1+K^n-nK)\right] \\ &= \chi_L(1+pK)/(1-pK),\end{aligned} \tag{25}$$

where $\chi_L = m^2\rho/3vkT = 2\lambda\rho/\pi$ is the Langevin initial susceptibility determining the magnetic response of the ideal paramagnetic gas of ferroparticles to an infinitely weak external field. The p value acts as the Lagrange parameter upon the minimization of free energy functional (2) in the absence of magnetic field, provided that the conditions of material balance (3) are fulfilled.

The density of chain particle number distribution is expressed via p

$$g_n(0) = \frac{p^n}{q_0}, \quad p = \frac{1+2q_0\rho-\sqrt{1+4q_0\rho}}{2q_0\rho} < 1. \tag{26}$$

Corresponding concentration dependence of parameter p is represented in Fig. 5. For low concentrated systems ($q_0\rho \ll 1$), we obtain $p \approx q_0\rho$ that implies the absence of aggregates. For a sufficiently large values of product $q_0\rho \sim 10$, this parameter increases very slowly (Fig. 5) taking values $p \approx 0.7$–0.8 and asymptotically tending to unity. Thus, the behavior of initial susceptibility (25) can be qualitatively represented as follows. At low concentrations, the susceptibility increases according to Langevin's law ($\chi \approx \chi_L$). Then follows the region of the linear rise of susceptibility. At rather high densities ($p \approx 1$), the linear rise with the slope larger than for Langevin's susceptibility is observed again $\chi \approx \chi_L (1 + K)/(1 - K)$.

Figures 6 and 7 demonstrate the concentration dependences of initial susceptibility (25) of the system of noninteracting chains for the four aforementioned regions of intrachain fluctuations. Successive rise of the susceptibility upon the passage from region (1) to region (3) is related with a considerable increase in the correlation coefficient (Fig. 4) at small decrease in the configuration integral (Fig. 3). A decrease in q_0 leads to some shortening of chains, which, however, are more rigid and are easier oriented in the external filed. The susceptibility sharply decreases in region (4) and acquires the value close to that found for region (1) despite the large correlation coefficient (Fig. 4, curve *4*). This is explained by much smaller values of q_0 (Fig. 3, curve *4*)

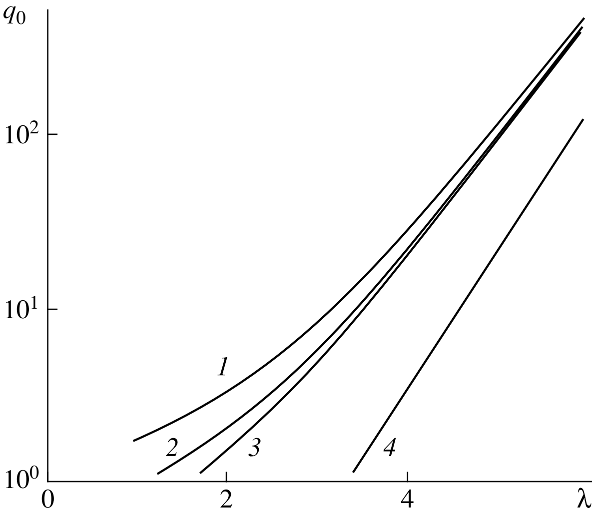

Fig. 3. Dependences of the configuration integral of doublet q_0 in the absence of magnetic field on the parameter of magnetodipole interaction λ for four regions (described in the text) of the account of intrachain fluctuations: (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 4.

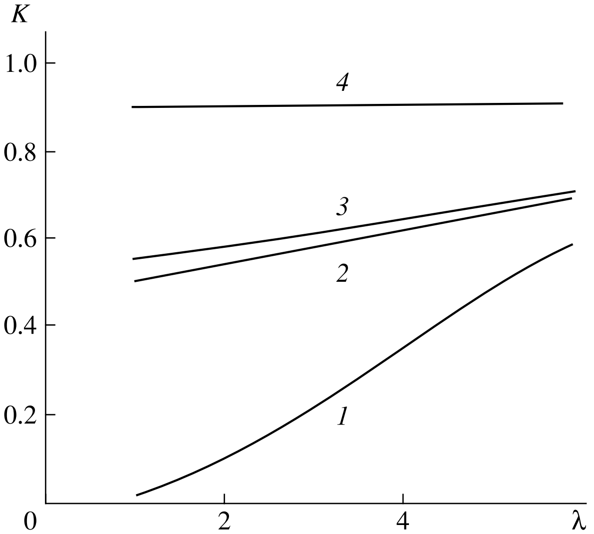

Fig. 4. Dependences of correlation coefficient K between the directions of the magnetic moments of neighbor particles in the chain on the parameter of magnetodipole interaction λ. Notations are the same as in Fig. 3.

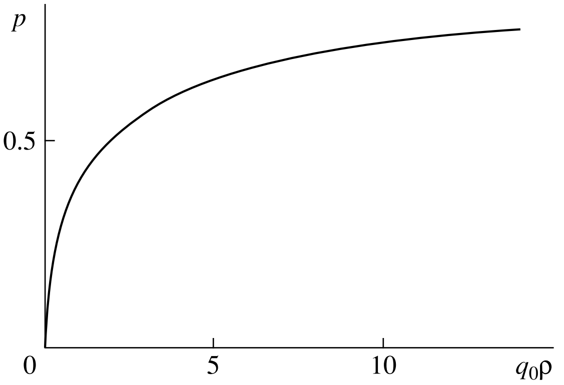

Fig. 5. Graphical representation of dependence (26).

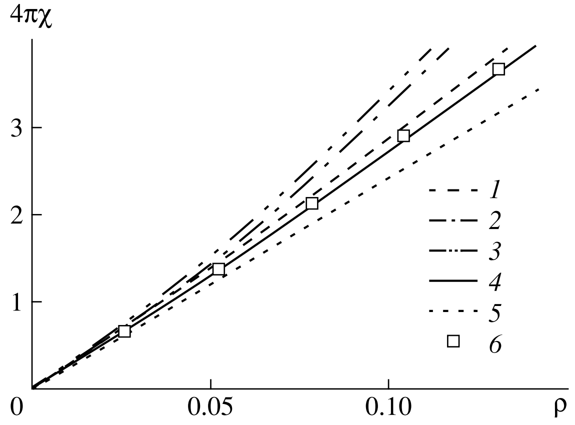

Fig. 6. Concentration dependences of the initial susceptibility of a system of noninteracting chains at λ = 3 for different regions of intrachain fluctuations: (*1*) 1, (*2*) 2, (*3*) 3, (*4*) 4, (*5*) Langevin susceptibility, and (*6*) the data of computer simulation [10].

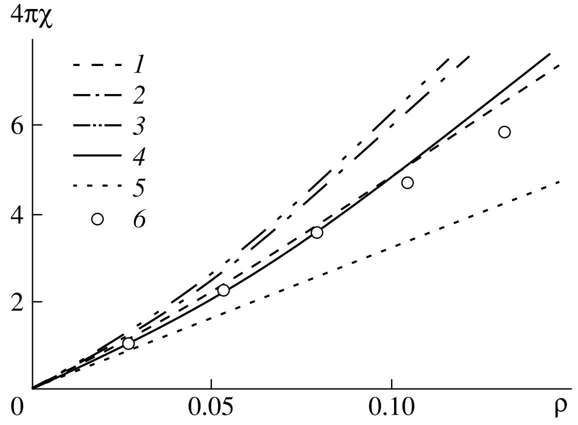

Fig. 7. Concentration dependences of the initial susceptibility of a system of noninteracting chains at λ = 4. Notations are the same as in Fig. 6.

and p in region 4. In fact, the number of chains is small in region (4) and they are short, although they can be considered as rodlike chains.

Figures 6 and 7 show also the data for Langevin effective susceptibility $4\pi\langle \rho m^2\rangle/3vkT$ obtained on the basis of computer simulation [10]; brackets denote the averaging over all chain aggregates. This value exceeds the susceptibility of the ideal gas of single particles χ_L, thus indicating the formation of chain clusters in a system already at low concentrations ($\rho \approx 0.05$). As is seen from Figs. 6 and 7, for the domains of integration (1) and (4), expression (25) quite adequately describes the data of computer simulation at low and moderate concentrations. The differences observed for λ = 4 (Fig. 7) at $\rho \approx 0.15$ (and larger) are, probably, related to the retardation of aggregate growth due to an increase in interchain interaction with the concentration, as was mentioned in [10]. At λ = 3, the number of chains is much smaller that is exhibited at higher concentrations. Therefore, in this case, the correspondence between the numerical and theoretical data is rather satisfactory also at $\rho \approx 0.15$ (Fig. 6).

6. CONCLUSIONS

In this work, we considered the behavior of a system of chain aggregates in a weak magnetic field. The analysis was performed on the basis of the free energy functional of a system. The formation of chain aggregates in a low concentrated magnetic fluid was studied; hence, interchain correlations were ignored. The interparticle dipole–dipole interaction of the magnetic moments of ferroparticles inside each chain was accounted only for the nearest neighbors. Under such assumptions that are traditional for the chain models of ferrofluids, we succeeded in calculating exactly the orientational correlations in chains caused by their interaction with weak uniform permanent external magnetic field. It was shown that the orientational response of chain aggregate to the magnetic field is determined by the coefficient of pair correlations of magnetic moments in a doublet of ferroparticles. The value of this coefficient depends on the orientational and spatial fluctuations admissible upon calculating the average interparticle bond energy inside the chain. Large values of the correlation coefficient corresponds to the orientational response that is typical of rigid rodlike particles; such a behavior is typical of doublets and triplets composed of large ferroparticles with a high intensity of magnetodipole interaction. The expressions derived make it possible to calculate also the response of long flexible chains to the weak magnetic field.

The degree of orientational rigidity turned out to be related with the number of aggregates. The assumption of strong intrachain correlations is unambiguously accompanied by the conclusion about their small number and length. In the case when chain aggregates are considered as flexible fluctuating structural elements, their number can be large enough; however, the rigid rod approximation becomes invalid for calculating the response to weak magnetic filed. Even for flexible chains in a low-concentration magnetic fluid, the susceptibility becomes substantially higher than that of the ideal paramagnetic gas. This result is consistent with the data of computer simulation of ferrofluids.

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