PHYSICAL REVIEW E **70**, 051502 (2004)

Ferrofluid aggregation in chains under the influence of a magnetic field

Valentin S. Mendelev and Alexey O. Ivanov*
Department of Mathematical Physics, Urals State University, 51 Lenin Avenue, Ekaterinburg 620083, Russia

(Received 8 June 2004; published 17 November 2004)

The theory of particle association in flexible chains in dilute ferrofluids is generalized to the case of an arbitrarily strengthened magnetic field. The chain distribution in dynamic equilibrium is obtained on the basis of free energy minimization method under the neglect of interchain interaction. The chain partition function is calculated analytically with the help of the rotation matrix technique under the condition when the interparticle dipole-dipole interaction between the nearest neighboring ferroparticles in each chain is taken into account. At weak fields, the chain distribution and the initial susceptibility are shown to be dependent on the value of the correlation coefficient describing the zero field mutual orientational correlations between the magnetic moments of two neighboring ferroparticles in a chain. The internal chain orientational correlations and the field dependent chain lengthening result in higher magnetization of the aggregated ferrofluid in comparison with the Langevin magnetization.

DOI: 10.1103/PhysRevE.70.051502 PACS number(s): 61.20.Gy, 75.50.Mm

I. INTRODUCTION

Magnetic fluids (ferrofluids, ferrocolloids) are suspensions of magnetic nanosized particles (Fe oxides, Co, Ni, etc.) covered by a solvent layer. The magnetic particles generally are approximately 10 nm in diameter. The ferro- or ferrimagnetic particles of such a size are single domain. So, each particle has its own magnetic moment $\mathbf{m}$, the value of which is proportional to the magnetic core volume and depends upon the saturation magnetization of the material. So, particles are not only involved in Brownian motion, but also interact with each other forming different aggregates. The rheological, hydrodynamic, diffusional, magnetic, and optical properties of a ferrofluid change by a hundred times under an applied magnetic field of moderate strength. So, such material is a challenging subject for scientific research as well as for different applications.

Recent computer simulations [1,2] have shown the microscopic structure of dipolar model fluids to be much more complex than previously expected. The system at a high dipolar strength and low volume fraction has proved to associate in chain aggregates, the number and length of which represent increasing functions of the ferroparticle concentration and of the strength of an external magnetic field. It is well known that magnetic fluids become optically anisotropic [3] and demonstrate an abrupt viscosity increase [4] when subjected to a magnetic field. The explanation of these phenomena is usually made in terms of chain aggregates. A lot of experimental studies, demonstrating not only chainlike aggregate existence but also their great influence upon diffusional and hydrodynamic properties of ferrofluids, are worth mentioning (see, for example, [5]).

The physical reason for the chain aggregate formation in ferrofluids is the pair interparticle magnetic dipole-dipole interaction $U_d(ij)$:

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

The latter is of noncentral character, since it depends not only on the distance r_{ij} between the ith and jth ferroparticles, but also on the mutual orientation of their magnetic moments $\mathbf{m}_i$ and $\mathbf{m}_j$. Hence, chain aggregates composed of ferroparticles the magnetic moments of which are in the most favorable energetic "head-to-tail" position prove to be typical for magnetic fluids. Naturally, these microstructures may be formed only by rather large ferroparticles, intensively interacting magnetically which each other. As a measure of such interaction the magnetic dipolar coupling constant $\lambda = m^2/d^3k_BT$ is usually used. This parameter represents the relation between the magnetic interaction energy of two contacting ferroparticles m^2/d^3 and the thermal energy k_BT (here d is the particle diameter taking account of the surface nonmagnetic and sterical layers). For real commercial ferrofluids the mean value of the dipolar coupling constant does not exceed unity. But a certain number of large sized particles (with diameters $\sim 15-18$ nm) always exists due to ferrofluid polydispersity. The dipolar coupling constant for these particles may reach values of $\lambda \sim 3-5$, which is rather high for establishing an interparticle "head-to-tail" bond. The microstructure of ferrofluids with the dipolar constant varied in this region was studied by means of molecular dynamics simulation [2]. According to these papers at low concentration the chain formation tends to increase the magnetization and induces a larger initial susceptibility. At high densities, the particle spatial distribution starts to homogenize again, and the significance of the chains goes down. This is due to the fact that in dense ferrofluids the interparticle interaction results in chain disintegration. The main conclusion of these papers was that the chain aggregates are most conspicuous in diluted ferrofluids, while dense ferrofluids are characterized by a homogeneous fluid like structure.

The computer simulations and experimental observations were accompanied by theoretical studies of the chain forma-

---

*Electronic address: Alexey.Ivanov@usu.ru tion process [6–10]. Two approaches for the chain aggregate description were proposed. The first one used the so-called dynamic method [6], where the particle combination/recombination processes in chains are treated as reversible chemical reactions. With the demand for dynamic equilibrium, the chain distribution as well as other important properties of the system could be obtained. The second commonly used approach is based on the minimization of the free energy as a functional of the chain distribution density [8–10]. So this method is called the density functional approach. The equivalence of these methods is an evident consequence of thermodynamic fundamentals. According to these works, a considerable fraction of ferroparticles at low densities and intensive magnetic dipole interaction is connected in chains, the mean length of which appears to be an increasing function of ferroparticle concentration. This approach was also extended to the case of polydisperse ferrofluids [11].

The general peculiarity of the models [9–11] is that only two limiting cases are studied: they are the zero field and the saturation conditions. However, the physical model of the ferrofluid chain aggregate microstructure is usually used for description of various properties induced by a magnetic field of moderate strength. Naturally, an external magnetic field stimulates chain formation. Unfortunately, no theoretical model properly describing the magnetic field influence upon the chain formation process has been built yet. The field orientation of stiff rodlike chain aggregates is the only known approach to take the magnetic field influence into account [8]. The rejection of chain flexibility results in the Langevin orientational law for each rodlike chain and leads to a great overestimation of the chain response to an external field. Therefore, the rigid rodlike chain approach should be considered only as a qualitative assumption, which is approximately valid for particles with high values of dipolar coupling constant.

This paper addresses the basic question of the ferrofluid chain behavior under the influence of an external magnetic field. In Sec. II the chain distribution is obtained on the basis of the density functional approach, and the rotation matrix technique is described. Since the chain distribution is dependent on the value of the chain partition function, its calculation is the main mathematical problem due to the necessity of averaging, that is integration, over a large number of the particle degrees of freedom. So, the averaging over the positions of particles (Sec. III) leads to some transformation of the chain partition function. An example given in Appendix A demonstrates this procedure for the system of dipolar hard spheres. The weak field asymptote is studied in Sec. IV, and the initial susceptibility of the aggregated ferrofluid is obtained. The detailed calculations are presented in Appendix B. Section V (and Appendix C as well) is devoted to the chain partition function in the presence of a moderate and/or strong magnetic field. Use of the saddle-point technique allows us to develop an asymptotic approach for analytical calculation of the chain partition function. The analytical expression appears to be very accurate in the whole region of magnetic field strength. The chain structure analysis and magnetization study are given in Sec. VI. We end with our conclusion in Sec. VII.

II. FREE ENERGY FUNCTIONAL

Let us consider a monodisperse ferrofluid, consisting of identical spherical ferroparticles of diameter d, volume $v=\pi d^3/6$, and magnetic moment m with volume concentration φ. The particles might be associated in chain aggregates, and the concentration of n-particle chains is g_n. It is well known [7] that under the presence of a magnetic field the thermodynamic properties of magnetic media are dependent on their shapes due to the demagnetization effects. Since we are going to study the microstructure and the magnetic properties of ferrofluids as functions of an external field, we choose the shape of the container with the ferrofluid such that the influence of the demagnetization field can be neglected. Thus, we consider the volume of the system in a shape of infinitely elongated ellipsoid of revolution (the ratio of the minor to major ellipsoid semiaxis tends to zero) stretched along an external uniform magnetic field $\mathbf{H}$. It is important to stress that using the infinitely elongated ellipsoidal shape is of advantage because this is just the case when the demagnetization factor is of no consequence and does not need to be accounted for (the external magnetic field coincides exactly with the internal one). For more general shapes of the container, the demagnetization factor of the system needs to be taken into account.

To use the energy density functional method the following assumptions are traditionally adopted: (i) Each chain is assumed to be a single structural element having its own translational and rotational degrees of freedom; (ii) structures that differ from those of chains are ignored; (iii) only the interaction between the nearest neighboring particles in every chain is taken into account; (iiii) diluted ferrofluids are studied ($\varphi \ll 1$), which is why an interaction between chains is not considered. Under these assumptions the free energy volume density F is the sum of the following terms: the ideal paramagnetic gas free energy F_m, the free energy of the chain ideal gas mixture, and the energy of each chain,

$$F = F_m + k_B T \sum_{n=1}^{\infty} g_n(H)\left(\ln \frac{g_n(H) v}{\mathrm{e}} - \ln Q_n(H)\right),$$

$$F_m = -k_B T \frac{\varphi}{v} \ln\left(\frac{\sinh \alpha}{\alpha}\right), \quad \alpha = \frac{mH}{k_B T}. \tag{2}$$

Here Q_n stands for the n-particle chain partition function; and α has the meaning of the Langevin parameter. The final problem is to find the minimum of the free energy (2) as a functional of the chain distribution g_n under the mass balance condition

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

and the solution should be written in the form

$$g_n(H) = p(H)^n Q_n(H)/v, \quad \sum_{n=1}^{\infty} n p(H)^n Q_n(H) = \varphi, \tag{4}$$

where the Lagrange multiplier $p(H)$ is to be determined numerically from the last algebraic equation. It is worth mentioning that the application of the model (2)–(4) is limited in major part by the neglect of interchain interactions. The latter cannot be linked only to the low density but also to the magnitude of the dipolar interactions and of the external field. For high fields and intensive dipolar interactions ($\lambda \sim 10$ and higher) one expects the appearance of ordered chain phases (nematic, columnar), as can be seen, for example, in Ref. [12]. Such structures are observed in magnetorheological suspensions at strong fields. In these suspensions of micrometer sized magnetic particles the dipolar coupling constant may amount to the values $\lambda \sim 10-50$. So, to use the model (2)–(4) we restrict our consideration to the region $\lambda \sim 3-5$, which is typical for the coarse grained fractions in real ferrocolloids with nanometer sized ferroparticles. Besides that, we study only low concentration ferrofluids as previously noted.

To use the chain distribution (4) one needs to calculate the chain partition function Q_n representing the averaged Gibbs distribution. In general, under the nearest neighbor condition the partition function of the n-particle chain is

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

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

$$U_m = \sum_{i=1}^{n} U_m(i) = -\sum_{i=1}^{n} (\mathbf{m}_i \cdot \mathbf{H}), \quad Q_1 = 1. \tag{5}$$

Here $d\tau_i$ stands for the differential volume element for the position and dipole orientation of the ith particle in a chain; the particle volume v plays the part of a normalizing coefficient; $U_d(ii+1)$ denotes the magnetic dipole-dipole interaction potential between two nearest neighboring particles in a chain; as far as the potential $U_s(ii+1)$ is concerned, it stands for a central interparticle interaction (steric repulsion, van der Waals attraction, electrostatic repulsion in ionic stabilized ferrofluids), and U_m describes the interaction of all particles with a magnetic field $\mathbf{H}$.

Since consideration is limited to chain aggregates, a most convenient coordinate system (Fig. 1) is one in which the position and orientation of the ith particle are specified by its relationship to the previous $(i-1)$th monomer unit in the chain. In this case [6], the radius vector $\mathbf{r}_{i-1i}$ connecting the centers of both particles and the magnetic moment of the ith particle are defined with the help of the rotation matrices $\mathbf{R}_i$ and $\mathbf{T}_i$:

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

$$\mathbf{R}_i = \begin{pmatrix} \cos\,\theta_i \cos\,\phi_i & -\sin\,\phi_i & \sin\,\theta_i \cos\,\phi_i \\ \cos\,\theta_i \sin\,\phi_i & \cos\,\phi_i & \sin\,\theta_i \sin\,\phi_i \\ -\sin\,\theta_i & 0 & \cos\,\theta_i \end{pmatrix}.$$

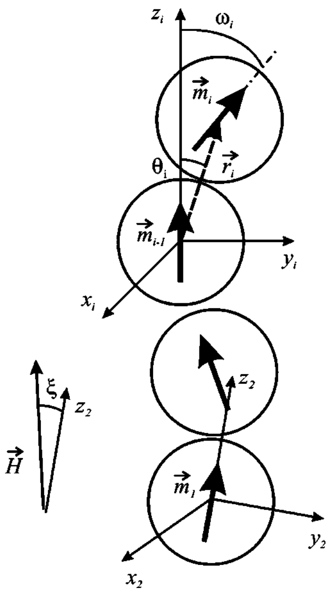

FIG. 1. Flexible chain and coordinate systems. The position and the dipole orientation of the ith particle are specified by its relationship to the previous $(i-1)$th monomer unit in the chain. The point of origin of the ith coordinate system is placed at the center of particle $i-1$ so that the Oz_i axis is codirectional to the $(i-1)$th magnetic moment.

$$\mathbf{T}_i = \begin{pmatrix} \cos\,\omega_i \cos\,\zeta_i & -\sin\,\zeta_i & \sin\,\omega_i \cos\,\zeta_i \\ \cos\,\omega_i \sin\,\zeta_i & \cos\,\zeta_i & \sin\,\omega_i \sin\,\zeta_i \\ -\sin\,\omega_i & 0 & \cos\,\omega_i \end{pmatrix}. \tag{6}$$

Each ith coordinate system point of origin is replaced in the center of the $(i-1)$th particle, and the Oz_i axis is directed along the $(i-1)$th magnetic moment (Fig. 1). So the orientation of the latter in the ith coordinate system is determined by the unit vector

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

In expressions (6) the vector $\mathbf{r}_i(r_i;\theta_i;\phi_i)$ connects the centers of the $(i-1)$th and ith particles in a chain $(i=2,\ldots,n)$; the unit vector $\boldsymbol{\Omega}_i(\omega_i;\zeta_i)$ determines the direction of the ith magnetic moment $(\mathbf{m}_i = m\boldsymbol{\Omega}_i)$. In terms of a coordinate system based on the position and dipole orientation of particle 1, expression (6) becomes, by successive rotations,

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

and the magnetic field is

$$\mathbf{H} = H\begin{pmatrix} \sin\,\xi \\ 0 \\ \cos\,\xi \end{pmatrix}. \tag{8}$$

With the help of this rotation matrix technique the partition function Eq. (5) is then

$$Q_n(H)=\left(\frac{\alpha}{\sinh\alpha}\right)^n\int_0^\pi\frac{\sin\xi d\xi}{2}\int\prod_{i=2}^n\frac{d\mathbf{r}_i}{v}\times\int\prod_{i=2}^n d\mathbf{\Omega}_i\exp\left(-\frac{U_s+U_d+U_m}{k_BT}\right),$$

$$d\mathbf{\Omega}_i=(4\pi)^{-1}\sin\omega_i d\omega_i d\zeta_i,\quad d\mathbf{r}_i=r_i^2dr_i\sin\theta_i d\theta_i d\phi_i, \tag{9}$$

where the integrations $d\mathbf{r}_i$ and $d\mathbf{\Omega}_i$ correspond to averaging over all particle positions and orientations in the chain with respect to normalization in the space of particle degrees of freedom, and the integration $\sin\xi d\xi/2$ stands for normalized averaging over all orientations of the flexible chain in a ferrofluid volume. This expression for the partition function was first suggested in Ref. [6]. The peculiar feature of these coordinate systems is that in each interparticle dipole-dipole interaction (1) the orientation of the ith magnetic moment is defined by the unit vector $\mathbf{n}$. On the other hand, the magnetic part of the interaction energy becomes complicated:

$$-U_m/k_BT=\alpha\sum_{i=1}^n Z_i, \tag{10}$$

where the functions Z_i are described by the recurring expressions

$$Z_i=X_{i-1}\sin\omega_i\cos\zeta_i+Y_{i-1}\sin\omega_i\sin\zeta_i+Z_{i-1}\cos\omega_i,$$

$$X_i=X_{i-1}\cos\omega_i\cos\zeta_i+Y_{i-1}\cos\omega_i\sin\zeta_i-Z_{i-1}\sin\omega_i,$$

$$Y_i=-X_{i-1}\sin\zeta_i+Y_{i-1}\cos\zeta_i,\quad 2\leqslant i\leqslant n,$$

$$X_1=\sin\xi,\quad Y_1=0,\quad Z_1=\cos\xi,\quad X_i^2+Y_i^2+Z_i^2=1. \tag{11}$$

The partition function (9) becomes simpler in two limiting cases: the zero field ($\alpha=0$) and saturation ($\alpha\to\infty$) conditions. Successive integrations over particle degrees of freedom result in the factorization features

$$Q_n(0)=q_0^{n-1},\quad q_0=\int\frac{d\mathbf{r}_2}{v}\int d\mathbf{\Omega}_2\times\exp\left(-\frac{U_d(12)+U_s(12)}{k_BT}\right),\quad \mathbf{m}_1=m\mathbf{n}, \tag{12}$$

$$Q_n(\infty)=q_\infty^{n-1},\quad q_\infty=\int\frac{d\mathbf{r}_2}{v}\exp\left(-\frac{U_d(12)+U_s(12)}{k_BT}\right), \tag{13}$$

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

In an arbitrarily strengthened external field this factorization of the partition function is absent, because the interaction between the particle magnetic moments and an external field leads to interparticle orientational correlations between all particles in a chain. That is why the problem of chain structure under the presence of a magnetic field has not been solved yet.

III. UNCOUPLING OF THE PARTITION FUNCTION

The analysis of expression (9) shows that the integration over the translational $d\mathbf{r}_i$ and orientational $d\mathbf{\Omega}_i$ variables should be uncoupled. In the integrand (9) all the functions Z_i are independent on the angles θ_i,ϕ_i, and only the dipole-dipole potentials $U_d(i-1i)$ are functions of these angles:

$$-\frac{U_d(i-1i)}{k_BT}=\lambda\left(\frac{d}{r_i}\right)^3[\cos\omega_i(3\cos^2\theta_i-1)+3\sin\omega_i\sin\theta_i\cos\theta_i\cos(\phi_i-\zeta_i)]. \tag{14}$$

Since we are interested in the integration of dipole-dipole potentials, the general transformation

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

allows us to use the dipole-dipole interaction potential in the form

$$-\frac{U_d(i-1i)}{k_BT}=\lambda\left(\frac{d}{r_i}\right)^3[\cos\omega_i(3\cos^2\theta_i-1)+3\sin\omega_i\sin\theta_i\cos\theta_i\cos\phi_i], \tag{15}$$

which does not contain the angles ζ_i. This means that the integrand $\exp[-(U_s+U_d)/k_BT]$ should be averaged over variables $d\mathbf{r}_i$ independently. Since the particle magnetic moments are correlated in a chain, this integrand has a sharp maximum of the height $\exp(2\lambda)\gg 1$ at the point $r_i=d$, $\theta_i=0$, $\omega_i=0$. On the basis of the saddle-point technique the following transformation approximately holds true:

$$\int\frac{d\mathbf{r}_i}{v}\exp\left(-\frac{U_s(i-1i)+U_d(i-1i)}{k_BT}\right)=q_\infty\exp[a(\cos\omega_i-1)],\quad \exp(2\lambda)\gg 1, \tag{16}$$

where the coefficients a and q_∞ depend on the dipolar coupling constant λ and on the form and intensity of the central interaction $U_s(ij)$. It is worth mentioning that the zero field partition function q_0 of the ferroparticle doublet should be determined with the help of parameters a and q_∞:

$$q_0=q_\infty\int d\mathbf{\Omega}_1\exp[a(\cos\omega_1-1)]=q_\infty\frac{1-\exp(-2a)}{2a}. \tag{17}$$

For example, $a=\lambda/2$, $q_\infty=\exp(2\lambda)/3\lambda^2$, $q_0=\exp(2\lambda)[1-\exp(-\lambda)]/3\lambda^3$ for dipolar hard spheres (see Appendix A). After that, the partition function should be written as

$$Q_n(\alpha)=q_\infty^{n-1}\left(\frac{\alpha}{\sinh\alpha}\right)^n\int_0^\pi\frac{\sin\xi\, d\xi}{2}\prod_{i=2}^n\int d\mathbf{\Omega}_i\times\exp[a(\cos\omega_i-1)]\exp\left(\alpha\sum_{j=1}^n Z_j\right). \tag{18}$$

The main idea of this uncoupling is the decrease of the integration variables. In expression (9) the number of these variables is equal to $1+5(n-1)$, and in expression (18) this number reduces to $1+2(n-1)$.

IV. WEAK FIELD LIMIT

The weak field response of the aggregated ferrofluid is of great interest since it allows us to calculate the initial magnetic susceptibility. For a weak magnetic field ($\alpha \ll 1$) the partition function (18) should be transformed by using the Taylor series expansion:

$$\exp\left(\alpha\sum_{j=1}^{n} Z_j\right) \approx 1 + \frac{\alpha^2}{2}\left(\sum_{j=1}^{n} Z_j\right)^2 = 1 + \frac{\alpha^2}{2}\sum_{j=1}^{n} Z_j^2 + \alpha^2 \sum_{k<j=1}^{n} Z_k Z_j, \qquad (19)$$

where the linear in α term vanishes due the symmetry of the problem. The calculations given in Appendix B show that in a weak field the partition function depends on the zero field correlation coefficient K, describing the averaged projection of one magnetic moment in a ferroparticle doublet onto the direction of the other:

$$Q_n(\alpha \ll 1) = q_0^{n-1}\left(\frac{\alpha}{\sinh \alpha}\right)^n \times \left[1 + \frac{\alpha^2}{6}\left(n + 2\frac{K}{(1-K)^2}(n-1+K^n-nK)\right)\right]. \qquad (20)$$

Using expression (16) in the definition of the correlation coefficient (B5), we get

$$K = L(a) \equiv \coth a - 1/a, \qquad (21)$$

where $L(a)$ stands for the Langevin function. It means that the correlation coefficient reaches the maximum allowable value, that is unity, in the limit of a highly intensive dipole-dipole interaction $K \to 1$, $\lambda \gg 1$. The combination

$$\langle m_n \rangle = \sqrt{n + 2\frac{K}{(1-K)^2}(n-1+K^n-nK)}, \qquad (22)$$

evidently, has the meaning of a dimensionless mean squared magnetic moment of the n-particle chain. For the rigid rodlike chain ($K=1$) it is $\langle m_n \rangle = n$, and the partition function coincides with that suggested in Ref. [8]:

$$Q_n(\alpha \ll 1) = q_0^{n-1}\left(\frac{\alpha}{\sinh \alpha}\right)^n \left(1 + \frac{\alpha^2 n^2}{6}\right) = q_0^{n-1}\left(\frac{\alpha}{\sinh \alpha}\right)^n \frac{\sinh \alpha n}{\alpha n}, \quad \alpha n \ll 1. \qquad (23)$$

The relation $\langle m_n \rangle / n$ is presented in Fig. 2 as a function of the correlation coefficient K. This figure shows that the chain might be considered as a rigid one ($\langle m_n \rangle / n \sim 0.9$ and higher) only for rather large values of the correlation coefficient ($K > 0.9$). The short chains (doublets and triplets) become rigid at lower values of K than long ones do. This is due the fact that in long chains the part of flexibility is more important than in the case of short ones.

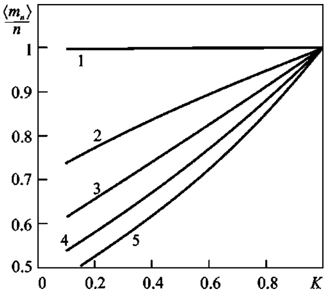

FIG. 2. Dependence of the relative mean squared magnetic moment $\langle m_n \rangle / n$ of an n-particle chain on the correlation coefficient K. Figures on the curves stand for the number n of ferroparticles in the chain.

The obtained expression for the partition function (20) allows us to calculate the initial magnetic susceptibility χ of the aggregated ferrofluid:

$$\chi = \frac{m^2}{k_B T}\sum_{n=1}^{\infty} g_n(0)\left(n + 2\frac{K}{(1-K)^2}(n-1+K^n-nK)\right) = \chi_L \frac{1+p_0 K}{1-p_0 K},$$

$$g_n(0) = \frac{p_0^n}{q_0 v}, \quad p_0 = \frac{1+2q_0\varphi - \sqrt{1+4q_0\varphi}}{2q_0\varphi} < 1, \qquad (24)$$

where $\chi_L = m^2\varphi/3vk_BT = 2\lambda\varphi/\pi$ stands for the Langevin susceptibility, and the Lagrange parameter p_0 defines the zero field chain distribution $g_n(0)$. For low concentration ferrofluids ($q_0\varphi \ll 1$) it follows that $p_0 \approx q_0\varphi$, $g_1(0) \approx \varphi/v$, and this means that the system is nonaggregated. In the region of the product values $q_0\varphi \sim 1-10$ the Lagrange parameter p_0 rapidly increases to the values $p_0 \sim 0.7-0.8$, and with the further increase of $q_0\varphi$ it slowly tends to unity. According to this behavior of p_0 the concentration dependence of the initial magnetic susceptibility χ (24) is the following. It linearly increases according to the Langevin law ($\chi \approx \chi_L \sim \varphi$) at very low concentrations. Then it grows nonlinear. And for rather large concentration ($p_0 \sim 0.9-1$) the susceptibility also increases linearly in φ, but the slope angle is larger than for the Langevin susceptibility $[\chi \approx \chi_L(1+K)/(1-K)]$. This concentration behavior of the initial susceptibility (24) is demonstrated in Figs. 3(a) and 3(b) in comparison with the Langevin susceptibility χ_L for dipolar coupling constants $\lambda=3$ (a) and 4 (b). The result of the rigid rodlike chain model [8] for the initial susceptibility also follows from the expression (24) under the condition when the correlation coefficient is equal to unity: $K=1$, $\chi = \chi_L(1+p_0)/(1-p_0)$. The last expression is also presented in Figs. 3(a) and 3(b). The boxes demonstrate the data of the molecular dynamics simulations [13] for the initial susceptibility of the system of noninteracting chains. The rejection of internal chain orientational fluctuations in the rigid rodlike chain model [8] leads to a great overestimation of the initial susceptibility (and magnetiza-

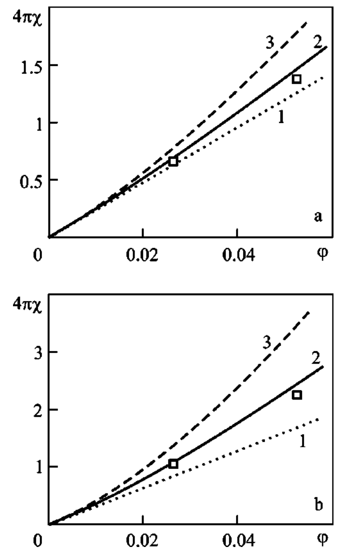

FIG. 3. (a) Concentration dependence of the initial susceptibility $4\pi\chi$ (24) (solid curve 2) in comparison with the Langevin susceptibility $4\pi\chi_L$ (dotted curve 1) and with the initial susceptibility in the rigid rodlike chain model (dashed curve 3) for a hard sphere ferrofluid with $\lambda = 3$; (b) the same dependencies as in (a) for $\lambda = 4$. The molecular dynamics data [13] are presented by boxes.

tion as well) in comparison with the present flexible chain theory and with the computer simulation data. The point is that the account of the chain flexibility is very important for proper description of computer and experimental studies of the magnetic properties of aggregated ferrofluids. And even for diluted ferrofluids the presence of flexible chain aggregates leads to higher values of the initial magnetic susceptibility as compared with the Langevin one.

V. MODERATE AND STRONG MAGNETIC FIELDS

For the case of an arbitrarily strengthened external field the evaluation of $Q_n(H)$ requires further approximations, valid as long as $\exp(2\lambda) \gg 1$. As shown in Appendix C, an asymptotic approximation of Eq. (9) yields

$$Q_n(\alpha) = q_\infty^{n-1} D_{n-1}(\alpha) \prod_{j=1}^{n-1} C_j(\alpha),$$

$$D_{n-1}(\alpha) = \frac{\alpha}{\sinh\,\alpha} \frac{\sinh[\alpha(1 + aB_{n-1})]}{\alpha(1 + aB_{n-1})},$$

$$C_j(\alpha) = \frac{\alpha}{\sinh\,\alpha} \frac{\sinh A_j}{A_j} \exp[-a(1 + \alpha B_j)], \quad A_j = \alpha f_j + a,$$

$$B_j = f_j L(A_j)/A_j,$$

$$f_{j+1} = 1 + a f_j L(\alpha f_j + a)/(\alpha f_j + a), \quad f_1 = 1. \tag{25}$$

Here the recurring coefficients $f_j \geq 1$ take into account the effect of superposed magnetization. It means that each particle is orientationally influenced by an effective field αf_i instead of the external one α. This effective strengthening of the field, acting on each particle in a chain, is connected with the mutual orientational correlations due to the influence of dipole-dipole interactions. The orientational response of one particle stimulates an additional reaction of the rest, since the dipole-dipole interaction tends to align the particle magnetic moments in a chain. In this sense, the recurring coefficients f_j define the effectively acting magnetic field.

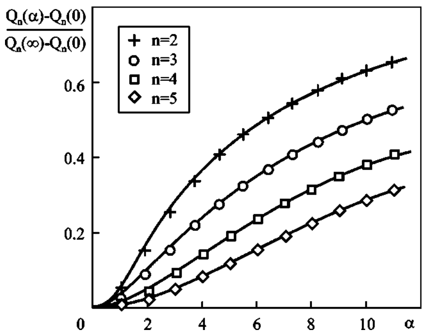

FIG. 4. Field dependence of the n-particle chain partition function $Q_n(\alpha)$ for dipolar hard spheres in comparison with the numerical calculations (points) for $\lambda = 4$.

The approximate expression (25) is examined with the help of numerical calculation of the n-particle chain partition function (18) for dipolar hard spheres $(n = 2, \ldots, 5)$, and the results are illustrated in Fig. 4 for $\lambda = 4$. The analytical expression (25) agrees well with the numerical data in the whole range of dimensionless magnetic field α; small deviations appear in weak fields. In addition, Fig. 4 demonstrates that the longer the chain is, the lower is the field growth rate of the chain partition function. This evident result is caused by the fact that in long chains the role of flexibility is more important than in the case of short ones.

At weak fields, the partition function (25) coincides with (12):

$$Q_n(\alpha = 0) = \left(q_\infty \frac{1 - \exp(-a)}{2a} \right)^{n-1} \equiv q_0^{n-1}. \tag{26}$$

Moreover, the strong field asymptote of the expression (25) demonstrates the factorization in the form

$$Q_n(\alpha \gg 2a) = [q_\infty/(1 + 2a/\alpha)]^{n-1}. \tag{27}$$

The analysis shows that this saturation asymptote is actually valid beginning from fields $\alpha \sim 10$.

The described algorithm of the partition function calculation may be easily extended to the case of polydisperse ferrofluids [11], as well as to the account of interparticle interaction between all particles in a chain without restriction to nearest neighbors. The last case will lead to an evident minor increase of the partition function, and this has an insignificant influence on further results.

VI. CHAIN AGGREGATE STRUCTURE IN A MAGNETIC FIELD

The combination of the calculated partition function (25) and general solution (4) allows us to study the chain aggre-

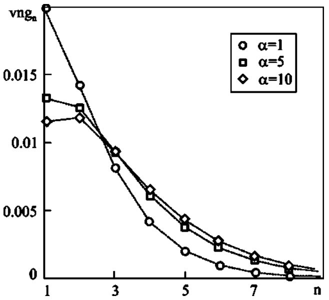

FIG. 5. Volume density vng_n of the n-particle chains in hard sphere ferrofluids for $\lambda=4$, $\varphi=0.05$ and various values of the dimensionless magnetic field $\alpha=1,5,10$.

gate structure under the influence of an external magnetic field of arbitrary strength. The dependence of the chain volume concentration vng_n on the number n of particles in a chain is shown in Fig. 5 for the hard sphere ferrofluid ($\lambda=4$, $\varphi=0.05$); the curves correspond to different values of the dimensionless magnetic field α. Naturally, field strengthening results in a shift of the chain distribution to the region of longer chains, and it means that the system considered becomes more aggregated. Such an influence is confirmed by the field dependence of the mean chain length $\langle n\rangle$, which is demonstrated in Fig. 6 for a diluted hard sphere ferrofluid with concentration $\varphi=0.05$. The mean chain lengthening is very intensive in the region of moderate magnetic fields $\alpha\sim 1-4$, and further field strengthening is accompanied by a slow approach of the ferroparticle system to the equilibrium chain distribution in saturation conditions.

With field growth the chains proved to be more rigid. This conclusion follows from the field behavior of the correlation coefficient $K(H)$, which is defined according to expression (B5) for nonzero magnetic field. On the basis of the method described in Appendix C the approximate simple dependence should be obtained:

$$K(H) \equiv K(\alpha) \approx L(\alpha + a), \tag{28}$$

which coincides with expression (21) for zero magnetic field. With field growth the correlation coefficient (28) monotonically increases and asymptotically reaches the maximum value, which is unity. When the dimensionless magnetic field is strong enough ($\alpha > 10$) the correlation coefficient takes values over 0.9. This means that the particle magnetic moments in a chain become codirectional, and the chain exhibits its rigid rodlike behavior in a magnetic field. In other words, a field strengthening leads to an evident weakening of the internal chain fluctuations. At first sight this conclusion is opposite to the theoretical [10] and numerical [14] predictions of globule formation. But in reality the chain-globule transition is possible only for rather long chains, containing dozens of ferroparticles. For the considered region of ferrofluid parameters ($\varphi \leqslant 0.05$, $\lambda \leqslant 5$) the presented model predicts the existence of relatively short chains (see Figs. 5 and 6). The obtained decrease of the flexibility of these short chains with field strengthening seems to be physically natural, and this effect does not contradict the globule formation of long chains [10,14].

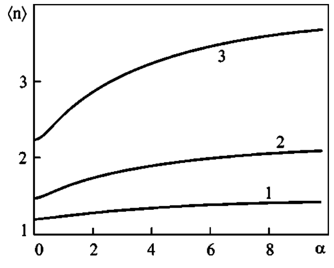

FIG. 6. Field dependence of the mean chain length $\langle n\rangle$ for a hard sphere ferrofluid with concentration $\varphi=0.05$. Curves 1–3 correspond to dipolar coupling constants $\lambda=3,4,5$.

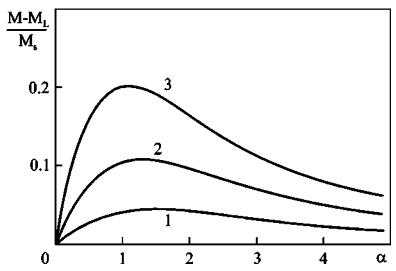

FIG. 7. Magnetization curves of aggregated hard sphere ferrofluids with ferroparticle concentration $\varphi=0.05$ and dipolar coupling constants $\lambda=3,4,5$ (curves 1–3, respectively). The difference between the magnetization M (29) and the Langevin magnetization M_L is presented for clarity.

The correlated orientational chain response to a magnetic field is accompanied by an increase of the magnetization M as compared with the Langevin magnetization M_L of an ideal paramagnetic gas of single ferroparticles. From the magnetization definition and the free energy volume density (2) it follows that

$$\begin{aligned} M(H) &= -\frac{\partial F}{\partial H} = M_s L(\alpha) + k_B T \sum_{n=1}^{\infty} g_n(H) \frac{\partial \ln Q_n(H)}{\partial H} \\ &= M_L(\alpha) + \frac{M_s}{\varphi} \sum_{n=2}^{\infty} p(\alpha)^n \frac{\partial Q_n(\alpha)}{\partial \alpha}, \end{aligned} \tag{29}$$

$$\sum_{n=1}^{\infty} n p(\alpha)^n Q_n(\alpha) = \varphi, \quad M_s = \frac{m\varphi}{v},$$

where M_s stands for saturation magnetization. The term additional to M_L takes into account the correlated contribution of all particles, associated in chains. It is worth noting that expression (29) is valid only for a system of noninteracting chains, similar to the ideal paramagnetic gas mixture of chains, the magnetic moments of which fluctuate inside the chains. But the magnetization of the last system proves to be higher than the Langevin magnetization due to the internal chain correlations. An additional influence is also exerted by chain lengthening in a magnetic field. The relative magnetization difference $(M-M_L)/M_s$ for the system of dipolar hard spheres is presented in Fig. 7 as a function of the Langevin parameter α for various values of dipolar coupling constant $\lambda=3,4,5$ and ferroparticle volume concentration $\varphi=0.05$.

The maximal excess lies in the region of moderate fields $\alpha \sim 1$ and increases with concentration φ. It should be pointed out that the effect of aggregated ferrofluid magnetization increase was reported in Ref. [2] and was unambiguously explained by the chain aggregate influence.

For strong magnetic fields the magnetization difference decreases parabolically $M-M_L \sim \alpha^{-2}$, and it follows from the asymptotical behavior (27). In other words, the magnetization (29) reaches the saturation value M_s according to the Langevin law $M=M_s(1-1/\alpha), \alpha \to \infty$. This fact is quite well substantiated physically, because the rapid growth of the aggregated ferrofluid magnetization in the region of weak and moderate magnetic fields (Fig. 7) is caused not only by the internal chain correlations but also by the chain lengthening (Fig. 6); whereas, in saturation fields the chain lengthening stops, and the magnetization behavior is determined by the single ferroparticle orientation only.

VII. CONCLUSION

In conclusion, the problem of equilibrium chain lengthening, caused by an external magnetic field, is solved analytically for the case of noninteracting flexible chains in low concentration magnetic fluid. The flexible chain orientational response to a magnetic field is shown to be weaker than for the rigid rodlike chains assumed in Ref. [8]. The last approximation holds true only for very high values of the dipole-dipole coupling constant.

Even for flexible chains, the obtained results demonstrate the great influence of the chain aggregates on the magnetostatic properties of ferrofluids due to orientational correlations between the magnetic moments of ferroparticles inside a chain. The amount of chain flexibility decreases with field strengthening, and in strong fields the chain aggregate resembles a stiff rodlike chain. Due to the existence and lengthening of chains, the magnetization and initial susceptibility of the aggregated ferrofluid turn out to be higher than those for a colloidal suspension of single ferroparticles. This conclusion is proved by the computer simulation data reported in Ref. [2]. At the same time, in computer simulations this effect was much more pronounced than is shown in Figs. 3 and 7. Apparently, it is caused by the interchain interactions, and the model should be extended to account for these interactions. Unfortunately, this makes it impossible to carry out an exact quantitative comparison at this time.

ACKNOWLEDGMENTS

The present research was carried out with the financial support of RFBR Grants No. DFG 03-02-04001, No. 04-02-16142, and No. 04-02-16078, INTAS Grant No. 03-51-6064, the President of Russian Federation Grant No. MD-336.2003.02 and "Universities of Russia" Grant No. ur.01.01.061. The research was also made possible in part by CRDF Award No. REC-005 (EK-005-X1).

APPENDIX A

As an example of the transformation (16) let us study the dipolar hard sphere system. So the central interparticle interaction $U_s(ij)$ is the hard sphere potential $U_{HS}(ij)$ of repulsion between particles of equal diameter d. Since the integrand in the partition function (9) has a sharp maximum of the height $\exp(2\lambda) \gg 1$ at the point $r_i=d$, $\theta_i=0$, $\omega_i=0$, a significant contribution should be found using the saddle-point technique. The expansion of the dipole-dipole potential (15) into Taylor series up to the second order terms gives $[r_i^3=d^3(1+x_i), x_i \ll 1, \theta_i \ll 1, \omega_i \ll 1]$

$$-U_d(i-1i)/k_BT = \lambda(2-2x_i-\omega_i^2-3\theta_i^2+3\omega_i\theta_i\cos\phi_i). \tag{A1}$$

Using the expanded dipole-dipole potential (A1) in the integrand (16), we get within the limits of the considered accuracy

$$\begin{aligned}\int \frac{d\mathbf{r}_i}{v}\exp\left[-\frac{U_{HS}(i-1i)+U_d(i-1i)}{k_BT}\right] &= \frac{2}{\pi}\int_0^\infty \theta_i d\theta_i \int_0^{2\pi} d\phi_i \int_0^\infty dx_i \\ &\quad \times \exp[\lambda(2-2x_i-\omega_i^2-3\theta_i^2+3\omega_i\theta_i\cos\phi_i)] \\ &= 2\frac{\exp(2\lambda)}{\lambda}\exp(-\lambda\omega_i^2)\int_0^\infty \theta_i d\theta_i \exp(-3\lambda\theta_i)I_0(3\lambda\theta_i\omega_i) \\ &= \exp(-\lambda\omega_i^2/4)\exp(2\lambda)/(3\lambda^2) \\ &= \exp[\lambda(\cos\omega_i-1)/2]\exp(2\lambda)/(3\lambda^2).\end{aligned} \tag{A2}$$

Here we use the integrals

$$\int_0^{2\pi}\exp(A\cos\phi)d\phi = 2\pi I_0(A),$$

$$\int_0^\infty \exp(-B\theta^2)I_0(C\theta)\theta\, d\theta = \exp(C^2/4B)/2B,$$

where $I_0(z)$ is the zero order modified Bessel function. The comparison of expressions (16) and (A2) allows us to write down (for the dipolar hard sphere fluid)

$$q_\infty = \exp(2\lambda)/(3\lambda^2), \quad a = \lambda/2. \tag{A3}$$

For the zero field partition function of the hard sphere ferroparticle doublet we get then

$$\begin{aligned} q_0 &= \frac{\exp(2\lambda)}{3\lambda^2}\int d\mathbf{\Omega}_i \exp[\lambda(\cos\omega_i-1)/2] \\ &= \frac{\exp(2\lambda)}{3\lambda^3}[1-\exp(-\lambda)].\end{aligned} \tag{A4}$$

The last expression coincides with the well known asymptote $q_0=\exp(2\lambda)/(3\lambda^3)$ [7] for high values of the dipolar coupling constant $\lambda \gg 1$.

APPENDIX B

Substitution of the weak field asymptote (19) allows us to integrate the partition function (9) over the angles ζ_i and ξ.

All diagonal elements Z_j^2 give the same contribution:

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

$$\int_0^\pi \frac{\sin\xi\,d\xi}{2}\int_0^{2\pi}\frac{d\zeta_2}{2\pi} Z_2^2 = \int_0^\pi \frac{\sin\xi\,d\xi}{4}[\sin^2\omega_2 + (3\cos^2\omega_2 - 1)Z_1^2] = \frac{1}{3},$$

$$\int_0^\pi \frac{\sin\xi\,d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{j}\frac{d\zeta_i}{2\pi} Z_j^2 = \int_0^\pi \frac{\sin\xi\,d\xi}{4}\int_0^{2\pi}\prod_{i=2}^{j-1}\frac{d\zeta_i}{2\pi} \times [\sin^2\omega_j + (3\cos^2\omega_j - 1)Z_{j-1}^2] = \frac{1}{3}.$$

In other words,

$$\int_0^\pi \frac{\sin\xi\,d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{n}\frac{d\zeta_i}{2\pi}\sum_{j=1}^{n} Z_j^2 = \frac{n}{3}. \qquad \text{(B1)}$$

Let us consider the cross elements $Z_kZ_j, k<j$, in expression (19):

$$\begin{aligned}\int_0^\pi \frac{\sin\xi\,d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{j}\frac{d\zeta_i}{2\pi} Z_kZ_j &= \int_0^\pi \frac{\sin\xi\,d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{j-1}\frac{d\zeta_i}{2\pi} Z_kZ_{j-1}\cos\omega_j \\ &= \int_0^\pi \frac{\sin\xi\,d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{k}\frac{d\zeta_i}{2\pi} Z_k^2\prod_{m=k+1}^{j}\cos\omega_m \\ &= \frac{1}{3}\prod_{m=k+1}^{j}\cos\omega_m.\end{aligned}$$

In all, the averaging of weak field expansion (19) for an n-particle chain over the angles ζ_i and ξ gives

$$\int_0^\pi \frac{\sin\xi\,d\xi}{2}\int_0^{2\pi}\prod_{i=2}^{n}\frac{d\zeta_i}{2\pi}\exp(-U_m/k_BT) \approx 1 + \frac{\alpha^2}{6}\left(n + 2\sum_{k<j=1}^{n}\prod_{m=k+1}^{j}\cos\omega_m\right). \qquad \text{(B2)}$$

Then, the weak field behavior of the partition function (9) is determined by the general formula

$$\begin{aligned}Q_n(\alpha \ll 1) = \frac{1}{v^{n-1}}\left(\frac{\alpha}{\sinh\alpha}\right)^n \int \prod_{i=2}^{n} d\mathbf{r}_i &\times \int_0^\pi \frac{\sin\omega_i\,d\omega_i}{2}\exp\left(-\frac{U_s + U_d}{k_BT}\right) \\ &\times \left[1 + \frac{\alpha^2}{6}\left(n + 2\sum_{k<j=1}^{n}\prod_{m=k+1}^{j}\cos\omega_m\right)\right], \end{aligned} \qquad \text{(B3)}$$

where all dipole-dipole potentials are defined by expression (15). The point is that this general formula is also factorable, since it represents the combinatorial sum of the independent items:

$$\begin{aligned}Q_n(\alpha \ll 1) &= q_0^{n-1}\left(\frac{\alpha}{\sinh\alpha}\right)^n\left[1 + \frac{\alpha^2}{6}\left(n + 2\sum_{k<j=1}^{n}K^{j-k}\right)\right] \\ &= q_0^{n-1}\left(\frac{\alpha}{\sinh\alpha}\right)^n\left[1 + \frac{\alpha^2}{6}\left(n + 2\frac{K}{(1-K)^2} \times (n - 1 + K^n - nK)\right)\right].\end{aligned} \qquad \text{(B4)}$$

Here we use the symbol K indicating the zero field correlation coefficient between the orientations of two neighboring particle magnetic moments in a chain:

$$K = q_0^{-1}\int \frac{d\mathbf{r}_2}{v}\int d\mathbf{\Omega}_2\cos\omega_2\exp\left(-\frac{U_d(12) + U_s(12)}{k_BT}\right). \qquad \text{(B5)}$$

With the help of expressions (16), (A3), and (A4) for a dipolar hard sphere fluid we obtain

$$K = L(\lambda/2) \equiv \coth(\lambda/2) - 2/\lambda.$$

APPENDIX C

The combination of expressions (9) and (16) allows us to write down the chain partition function in the following form, which is easy to use in the chain structure analysis under the presence of a strong and moderately strengthened external field:

$$Q_n(\alpha) = q_\infty^{n-1}\left(\frac{\alpha}{\sinh\alpha}\right)^n\int_0^\pi \frac{\sin\xi\,d\xi}{2} \times \exp(\alpha Z_1)\prod_{i=2}^{n}\int d\mathbf{\Omega}_i\exp(W_i),$$

$$W_i = -a + a\cos\omega_i + \alpha Z_i. \qquad \text{(C1)}$$

Let us successively integrate over the orientations of particle magnetic moments beginning from the last one. Using the recurring formulas (11), let us express W_n as

$$W_n = \widetilde{W}_n = -a + (\alpha f_n Z_{n-1} + a)\cos\omega_n + \alpha f_n(X_{n-1}\cos\zeta_n + Y_{n-1}\sin\zeta_n)\sin\omega_n, \quad f_n = 1.$$

After that, the integrals $d\mathbf{\Omega}_n$ should be calculated exactly:

$$J_n = \int d\mathbf{\Omega}_n \exp(\widetilde{W}_n) = \exp(-a)\int_0^{\pi} \frac{\sin \omega_n d\omega_n}{2}$$
$$\times \exp[(\alpha f_n Z_{n-1} + a)\cos \omega_n] I_0(\alpha f_n \sqrt{X_{n-1}^2 + Y_{n-1}^2} \sin \omega_n)$$
$$= \exp(-a)\frac{\sinh u_n}{u_n},$$
$$\times u_n^2 = a^2 + (\alpha f_n)^2 + 2a\alpha f_n Z_{n-1}. \qquad (C2)$$

In view of the fact that the chain is a correlated object, the function u_n has a sharp maximum at the point $Z_{n-1} \approx 1$. This allows us to expand

$$\frac{\sinh u_n}{u_n} = \frac{\sinh(\alpha f_n + a)}{\alpha f_n + a} \exp\left(\frac{a\alpha f_n L(\alpha f_n + a)}{\alpha f_n + a}(Z_{n-1} - 1)\right). \qquad (C3)$$

Then

$$\int d\mathbf{\Omega}_{n-1} \exp(W_{n-1}) J_n = \frac{\sinh A_n}{A_n} \exp[-a(1 + \alpha B_n)] J_{n-1},$$

$$J_{n-1} = \int d\mathbf{\Omega}_{n-1} \exp(\widetilde{W}_{n-1}).$$

$$\widetilde{W}_{n-1} = -a + (\alpha f_{n-1} Z_{n-2} + a)\cos \omega_{n-1}$$
$$+ \alpha f_{n-1}(X_{n-2} \cos \zeta_{n-1} + Y_{n-2} \sin \zeta_{n-1})\sin \omega_{n-1},$$

$$A_n = \alpha f_n + a, \quad B_n = f_n L(A_n)/A_n,$$
$$f_{n-1} = 1 + a f_n L(\alpha f_n + a)/(\alpha f_n + a), \qquad (C4)$$

where the functions $\widetilde{W}_i$ differs from W_i [Eq. (C1)] by the recurring coefficients $f_i \geqslant 1$. The preceding arguments may now be repeated sequentially with the result

$$\int_0^{\pi} \frac{\sin \xi \, d\xi}{2} \exp(\alpha Z_1) \prod_{i=2}^{n} \int d\mathbf{\Omega}_i \exp(W_i)$$
$$= \prod_{i=2}^{n} \frac{\sinh A_i}{A_i} \exp[-a(1 + \alpha B_i)] \int_0^{\pi} \frac{\sin \xi \, d\xi}{2}$$
$$\times \exp[\alpha(1 + aB_2)\cos \xi]$$
$$= \frac{\sinh[\alpha(1 + aB_2)]}{\alpha(1 + aB_2)} \prod_{i=2}^{n} \frac{\sinh A_i}{A_i} \exp[-a(1 + \alpha B_i)].$$

In the last expression the recurring calculation of the coefficients A_i, B_i should be done beginning from the last particle of the index n up to the second one. Summation from the first particle (see Fig. 1) seems to be more convenient. So the summation index i is replaced by $j = n - i + 1$ in the final expression (25) for the n-particle chain partition function.

[1] M.E. van Leeuwen and B. Smit, Phys. Rev. Lett. **71**, 3991 (1993); M. J. Stevens and G. S. Grest, Phys. Rev. E **51**, 5962 (1995); A. Satoh *et al.*, J. Colloid Interface Sci. **178**, 620 (1996); G. N. Coverdale *et al.*, J. Magn. Magn. Mater. **188**, 41 (1998); Ph. J. Camp and G. N. Patey, Phys. Rev. E **62**, 5403 (2000); A. F. Pshenichnikov and V. V. Mekhonoshin, J. Magn. Magn. Mater. **213**, 357 (2000); Eur. Phys. J. E **6**, 399 (2001); T. Kristóf and I. Szalai, Phys. Rev. E **68**, 041109 (2003); T. Kruse, A. Spanoudaki, and R. Pelster, Phys. Rev. B **68**, 054208 (2003).

[2] Z. Wang, C. Holm, and H. W. Müller, Phys. Rev. E **66**, 021405 (2002); Z. Wang and C. Holm, *ibid.* **68**, 041401 (2003).

[3] Yu. N. Skibin, V. V. Chekanov, and Yu. L. Raikher, Sov. Phys. JETP **45**, 496 (1977); P. C. Scholten, IEEE Trans. Magn. **16**, 221 (1980); S. Taketomi, Jpn. J. Appl. Phys., Part 1 **1137**, 22 (1983); E. Hasmonay *et al.*, Eur. Phys. J. B **5**, 859 (1998); M. Rasa, J. Magn. Magn. Mater. **201**, 170 (1999); A. F. Pshenichnikov and V. M. Buzhmakov, Colloid J. **63**, 305 (2001); E. Hasmonay *et al.*, J. Appl. Phys. **88**, 6628 (2000).

[4] S. Odenbach and H. Gilly, J. Magn. Magn. Mater. **152**, 123 (1996); S. Odenbach and H. Stork, *ibid.* **183**, 188 (1998); S. Odenbach, *Magnetoviscous Effects in Ferrofluids*, Lecture Notes in Physics Vol. M71, Springer, Berlin, 2002).

[5] S. Kamiyama and A. Satoh, J. Colloid Interface Sci. **127**, 173 (1989); R. Rosman, J. S. M. Janssen, and M. Th. Rekveldt, J. Magn. Magn. Mater. **85**, 97 (1990); H. D. Williams, K. O'Grady, and S. W. Charles, *ibid.* **122**, 134 (1993); V. M. Buzmakov and A. F. Pshenichnikov, J. Colloid Interface Sci. **182**, 63 (1996).

[6] P. Jordan, Mol. Phys. **25**, 961 (1973); **38**, 769 (1979).

[7] P. G. de Gennes and P. Pincus, Phys. Kondens. Mater. **11**, 189 (1970).

[8] A. Yu. Zubarev and L. Yu. Iskakova, J. Exp. Theor. Phys. **80**, 857 (1995); A. Yu. Zubarev, *ibid.* **93**, 80 (2001); in *Ferrofluids, Magnetically Controllable Fluids and Their Applications*, Lecture Notes in Physics Vol. 594, by S. Odenbach (Springer, Berlin, 2002); A. O. Ivanov, Z. Wang, and C. Holm, Phys. Rev. E **69**, 031206 (2004).

[9] R. P. Sear, Phys. Rev. Lett. **76**, 2310 (1996); R. van Roij, *ibid.* **76**, 3348 (1996); M. A. Osipov, P. I.C. Teixeira, and M. M. Telo da Gama, Phys. Rev. E **54**, 2597 (1996); J. M. Tavares, J. J. Weis, and M. M. Telo da Gama, *ibid.* **59**, 4388 (1999).

[10] K. I. Morozov and M. I. Shliomis, in *Ferrofluids, Magnetically Controllable Fluids and Their Applications* [8].

[11] S. Kantorovich, J. Magn. Magn. Mater. **258-259**, 471 (2003); A. O. Ivanov and S. Kantorovich, Colloid J. **65**, 166 (2003); A. O. Ivanov and S. S. Kantorovich, Phys. Rev. E **70**, 021401 (2004).

[12] J.-J. Weis, J. Phys.: Condens. Matter **15**, S1471 (2003).

[13] Z. Wang and C. Holm (private communication).

[14] P. Rein ten Wolde, D. W. Oxtoby, and D. Frenkel, Phys. Rev. Lett. **81**, 3695 (1998).