Internal structures in two-dimensional ferrofluids

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We present the results of a theoretical study of internal microstructures in two-dimensional ferrofluids without an external magnetic field. Recent experiments with these systems demonstrate the appearance of linear chains and ringlike and various branched clusters. We consider linear chains, rings, and branched Y-like "forks." In the model of an ideal gas of noninteracting clusters, taking into account interactions only between nearest particles, we estimate the equilibrium distribution functions of the chains, forks, and rings over a number of particles in them. Our results show that for experimentally realistic situations the majority of particles are united into chains and forks, the number of particles in the rings being relatively small. The results of calculations are in qualitative agreement with experiments.

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I. INTRODUCTION

Ferrofluids, colloidally stable suspensions of magnetic subdomain particles in a carrier liquid, have attracted the considerable interest of researchers and engineers due to their rich set of physical properties valuable for modern high technologies. Many experiments (see, for example, Ref. [1]) demonstrate that if the temperature is low enough (however, around room temperature), and/or the external magnetic field is high enough, the particles condense into bulk dense drop-(column-) like aggregates. Theoretical models of these condensations, treated as the first kind of phase transitions, have been suggested in the works in Ref. [2]. Many computer simulations (see, for example, Ref. [3]) demonstrate the appearance of linear-chain-like aggregates in systems of dipole particles. Various theoretical investigations of these chains have been carried out in models [4]. The problem of the chain-drop transformation has been considered in Ref. [5].

In spite of rich experimental material and many theoretical investigations, including analytical models and computer simulations, the problem of the internal structures in ferrofluids is still discussed. The matter is that only bulk drops (columns) can be directly observed in experiments with three-dimensional (3D) systems. Optical observations of the chains are impossible since the diameter of the magnetic particles (10–20 nm) is less than the wavelength of visible light.

Recently the internal structures in two-dimensional monolayers of ferrofluids have been observed in experiments [6,7] by using cryogenic transmission electronic microscopy under conditions of zero [6] and strong [7] external field. The following types of structures have been detected in experiments [6]: (a) linear chains, (b) branched structures, consisting of linear chains, bounded with one or several ties, and (c) closed rings. No dense 2D spots, similar to the 3D drops, detected in experiments [1], have been observed in Ref. [6]. This disagreement between 3D and 2D experiments can be explained by the fact that the absolute magnitude of the effective energy of the dipole-dipole attraction of a particle with surrounding particles in 2D spots is less than that in 3D drops. Thus in 2D systems the energy of the particle interaction, which is necessary for surface condensation, must be significantly higher than the energy necessary for bulk condensation in the 3D samples. We think that in conditions of [6] the energy of interactions between particles was too small to provide their surface condensation. At the same time, possibly, in two-dimensional layers, unlike three-dimensional systems, without an applied magnetic field, a combination of entropic and energetic factors makes the appearance of the macroscopically homogeneous percolating net of chains segments more profitable than particle condensation into dense phases [8].

As is well known, in 3D systems an external magnetic field stimulates condensation of magnetic particles into bulk dense drops [1,2]. Condensation of the particles into dense 2D stripes, aligned along the applied magnetic field, has been detected in experiments [7].

In spite of quite different conditions of the particle aggregation in 2D and 3D systems, the monolayers of ferrofluids present significant interest and merit attentive consideration. The matter is, nowadays, that the monolayers are the only ferrofluid systems in which linear and branched structures can be observed directly.

The aim of this paper is a theoretical study of the chain, branched, and ring clusters in 2D monolayers of ferrofluids. The case of zero external field is considered. In the next section, Sec. III, we present a general statistical model for the determination of the functions of distribution over the number of particles in the chain, ring, and branched structures. This model includes the effective energy of bonds between particles in these structures. In Secs. III and IV and V we estimate the energies of these bonds in the chains, in the three-particle ties of the branched structures, and in the rings, respectively. Those readers who are not interested in the mathematical details of the these calculations can skip these parts and pass on to Sec. VI where we present some results of our calculations and their comparison with experiments.

We consider the ferrofluid as a system of identical magnetic balls with a permanent magnetic moment each. The particles can move in the plane of the monolayer, but cannot in the direction normal to this plane. In real systems the magnetic moments of the particles can fluctuate both in the layer plane and in the normal direction. For maximal simplification of calculations, we consider an entirely 2D system—i.e., suppose that the particle moments, like their disposi-

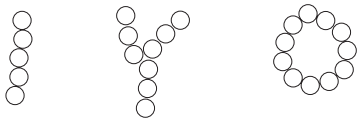

FIG. 1. Sketch of the linear chains and the Y-branched and ring clusters considered in this model.

tions, vary only in the plane of the monolayer. This means that we exclude the degree of freedom of the particle moments in the direction normal to the ferrofluid plane. This approximation overestimates the effective energy of the particle bonds in the clusters; however, it allows us to simplify greatly all calculations and final results. In more detail it is discussed in the Conclusion.

II. GENERAL MODEL OF THE CLUSTER SIZE DISTRIBUTION

We consider a 2D layer of a ferrofluid, consisting of identical magnetic particles. Let m be the particle magnetic moment and d_p the particle hydrodynamical diameter (with the surface layer on the particle). According to the results of observations of Ref. [6], we suppose that the particles are assembled only into linear chains, branched structures, and linear rings (see Fig. 1); i.e., we ignore the dense surface spots of the particles. Our goal is to find the distribution functions over the number of particles in these clusters. For maximal simplification of analysis we restrict ourselves to consideration of only the linear chains, closed rings and Y-type "forks" shown in Fig. 1. It should be noted that in the conditions of experiments [6] concentrations of clusters with other than the mentioned structures were quite small and, in the first approximation, can be neglected.

Let us denote by g_n^c and g_n^r the numbers of n-particle chains and rings per unit surface of the system, respectively. The Y-branched cluster can be considered as a combination of three linear chains. Assuming that the chains consist of i, j, and k particles, we denote the number of these clusters per unit surface of the system by g_{ijk}^Y.

In the nearest-neighbor approximation, which is quite accurate for linear or quasilinear structures [4], neglecting any interactions between different clusters, we can present the free energy of the unit surface of the system as

$$F = kT\left[\sum_{n=1}^{\infty}\left(g_n^c \ln\frac{g_n^c s}{e} - g_n^c(n-1)\varepsilon^c\right) + \sum_{n=5}^{\infty}\left(g_n^r \ln\frac{g_n^r s}{e} - g_n^r n\varepsilon_n^r\right) + \sum_{i\geqslant i\geqslant k=1}^{\infty}\left(g_{ijk}^Y \ln\frac{g_{ijk}^Y s}{e} - g_{ijk}^Y[(i+j+k-3)\varepsilon^c + \varepsilon^t]\right)\right],$$

$$s = \pi\frac{d_p^2}{4}. \tag{1}$$

The first terms in each sum of Eq. (1) are the entropies of the ideal gases of the chains, rings, and Y clusters, respectively. The second terms are the dimensionless free energies of the clusters due to a magnetic interaction between the nearest particles. The parameters ε^c, ε^t, and ε_n^r present the dimensionless, with respect to kT, free energies of the bonds between the particles in the chain, in the three-particle "tie," and in the ring, respectively. Unlike ε^c, the parameter ε_n^r depends on the number n of the particles in the ring. The explicit forms of the magnitudes ε^c, ε^t, and ε_n^r are presented below in Eqs. (14), (29), and (53), respectively. Here and below we start the summation for the rings with $n=5$ due to the fact that the probabilities of appearance of the closed triplets and quartets are much less than those for the linear chains consisting of three and four particles, respectively. This fact is discussed at the end of Sec. III. Moreover, the triplet is taken into account in the term with g_{111}^Y. The closed quartets are ignored here.

Justification of the approximation of the ideal gas of the noninteracting clusters with nearest-neighbor interactions inside them is discussed in the end of this part of work.

The equilibrium distribution functions g^c, g^r, and g^Y provide a minimum of free energy F under the following normalization condition:

$$\sum_{n=1}^{\infty} n g_n^c + \sum_{n=5}^{\infty} n g_n^r + \sum_{i\geqslant j\geqslant k=1}^{\infty}(i+j+k) g_{ijk}^Y = \frac{\Phi}{s}, \tag{2}$$

where Φ is the surface concentration (surface fraction) of the particles and the ratio $\nu=\Phi/s$ is the total number of particles per unit surface of the system. Minimization of F in (1) leads to the following expressions for the distribution functions:

$$g_n^c = \frac{1}{s}\exp[(n-1)\varepsilon^c + n\Lambda],$$

$$g_n^r = \frac{1}{s}\exp(n\varepsilon_n^r + n\Lambda),$$

$$g_{ijk}^Y = \frac{1}{s}\exp[(i+j+k-3)\varepsilon^c + \varepsilon^t + n\Lambda], \tag{3}$$

where Λ is the undetermined Lagrangian multiplier. In order to determine Λ, we should substitute Eq. (3) into the normalization condition (2) to give a transcendental equation for Λ, which can be solved numerically.

Having this equation solved, we can determine, in the framework of the chosen approximation, all equilibrium characteristics of the system.

Let p_0, p_1, p_2, and p_3 denote the probabilities of the fact that an arbitrary particle does not have any nearest neighbor (i.e., a single particle), has one neighbor particle (a particle in a doublet, end particle either in a chain or in branched cluster), has two neighbors (internal particle in a chain and in branches of Y cluster, particle in ring), and three nearest neighbors (particle in the tie of branched cluster). Simple considerations give

$$p_0 = g_1^c \nu^{-1},$$

$$p_1 = \left(2\sum_{n\geqslant 2}^{\infty} g_n^c + 3\sum_{i\geqslant j\geqslant k\geqslant 2}^{\infty} g_{ijk}^Y + 2\sum_{i\geqslant 2} g_{ij1}^Y + \sum_{i\geqslant 2} g_{i11}^Y \right) \nu^{-1},$$

$$p_2 = \left(\sum_{n\geqslant 3}^{\infty} (n-2) g_n^c + \sum_{i\geqslant j\geqslant k\geqslant 3}^{\infty} (i+j+k-6) g_{ijk}^Y + \sum_{i\geqslant j\geqslant 3}^{\infty} (i+j-4)(g_{ij1}^Y + g_{ij2}^Y) + \sum_{i\geqslant 3} (g_{i11}^Y + g_{i21}^Y + g_{i22}^Y) \right) \nu^{-1},$$

$$p_3 = \sum_{i\geqslant j\geqslant k\geqslant 1} g_{ijk}^Y \nu^{-1}. \tag{4}$$

Some results of calculations of the probabilities and their comparison with experiments of Ref. [6] are discussed in Sec. VI.

Let us return now to the justification of the model in Eq. (1) of the ideal gas of the clusters with interactions only between nearest particles in them. The matter is that experiments in Ref. [6] indicate that, in spite of the long-range character of the dipole-dipole interaction, the deviations of the cluster size distributions from exponential forms like Eq. (3) are weak even for particle concentrations of about 0.14. Computer simulations of the systems of dipole particles (see, for example, Ref. [9] and references there in) with concentration about 10% also demonstrate weak deviations of the distribution functions from the exponential laws even for high magnitudes of energy of the magnetic interaction between particles. It gives us an experimental background to consider the model of ideal gas of clusters with nearest-neighbor interactions in them as a quite adequate first approximation to study the pretransition state of the systems. It seems for us also that this approximation is a necessary first step for the development of more precise but much more cumbersome models.

III. EFFECTIVE ENERGY ε^c OF THE PARTICLE BOND IN THE CHAIN

Let us consider a linear chain consisting of n particles (Fig. 2). In the nearest-neighbor approximation the free energy of the chain can be presented as

$$f_n^c = -kT \ln Z_n^c = -kT(n-1)\varepsilon^c,$$

$$Z_n^c = \frac{1}{s^{n-1}} \int \exp(-U^c) d\mathbf{m}_2 \cdots d\mathbf{m}_n d\mathbf{r}_{12} \cdots \mathbf{r}_{n,n-1},$$

$$U^c = u_{12} + u_{23} + \cdots + u_{n-1,n}. \tag{5}$$

Here Z_n^c is the statistical integral of an n-particle linear chain, $u_{i,i+1}$ is the dimensional potential of the dipole-dipole interaction between the ith and jth particles in the chain, and $\mathbf{r}_{i,i+1}$ is the radius vector between centers of these particles.

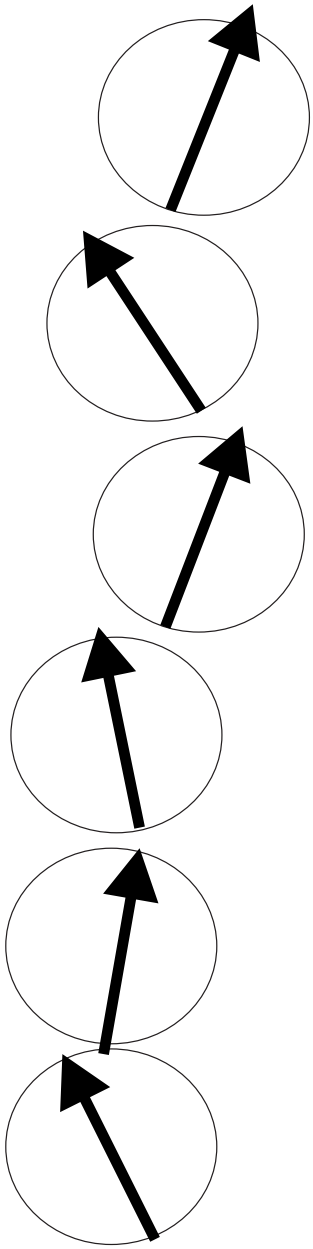

FIG. 2. Sketch of the chain with fluctuating positions of particles and their magnetic moments.

The well-known results of the theory of the chains of dipole particles in Ref. [4] allow one to factorize the integral in Eq. (5) and to present it as follows:

$$Z_n^c = (z^c)^{n-1},$$

$$z^c = \frac{1}{s} \int \exp(-u_{12}) d\mathbf{m}_2 d\mathbf{r}_{12}. \tag{6}$$

The dimensionless potential u_{12} of the dipole-dipole interaction between the nearest particles in the chain can be presented as

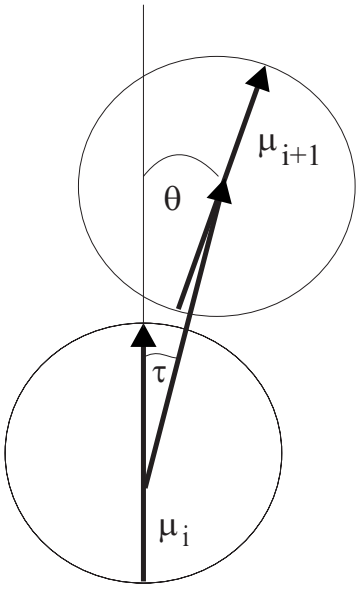

FIG. 3. Sketch of the polar coordinate system in the doublet of particles.

$$u_{12} = -\lambda\left(3\frac{(\mu_1\cdot\xi)(\mu_2\cdot\xi)}{\xi^5} - \frac{(\mu_1\cdot\mu_2)}{\xi^3}\right), \tag{7}$$

where the following dimensionless magnitudes are used:

$$\lambda = \frac{\mu_0}{4\pi}\frac{m^2}{kTd_p^3}, \quad \mu_{1,2} = \frac{\mathbf{m}_{1,2}}{m}, \quad \xi = \frac{\mathbf{r}_{12}}{d_p},$$

and μ_0 is the vacuum permeability.

One should perform the integration in Eqs. (5) and (6) in such a way as to provide the condition that the particles belong to the same chain. This leads us to a problem of a definition of the chain, i.e., to the question as to how large the distance can be between the particles provided that they belong to one chain. Of course, any choice of a sharp criterion for this threshold distance has an arbitrary character and one can suggest one's own criterion for the boundary distance. In order to avoid arbitrariness in the definition of the chain, here, as in the models in Ref. [4], we will use the saddle-point method discussed below.

Following to the main ideas of this method, let us consider two particles that feature in the integral z^c. We introduce a polar coordinate system with the origin in the center of the first particle of this doublet and the polar axis aligned along vector $\mathbf{m}_1$ (Fig. 3). We denote by θ and τ the angles between the vectors $\mathbf{m}_2$ and ξ and the polar axis, respectively. Taking into account the assumptions that all three vectors $\mathbf{m}_1$, $\mathbf{m}_2$, and ξ lie in the same plane, we can rewrite Eq. (7) as

$$u_{12} = -\lambda\frac{3\cos\tau\cos(\theta-\tau) - \cos\theta}{\xi^3}. \tag{8}$$

The main problem of integration in (6) is in the fact that this integral diverges when ξ tends to infinity. In order to overcome this problem, let us take into account that the term "chain" corresponds to a cluster in which the particles are situated quite close to each other and near their poles. Then, obviously, the chains and other clusters can exist only when the parameter λ of the dipole interaction between the particles is significantly more than unity. That is why the exponent in Eq. (6) has a sharp maximum near the point $\theta=\tau=0$, $\xi=1$. Following the saddle-point method, we expand the potential u_{12} in Eq. (8) as a power series in θ, τ and $x=\xi-1$. Assuming that these parameters are small—that is, consistent with the term "chain"—we get instead Eq. (8)

$$u_{12} \approx -2\lambda + \lambda\left[\frac{3}{2}\tau^2 + \frac{3}{2}(\theta-\tau)^2 + 6x\right]. \tag{9}$$

Combining Eqs. (9) with (6), we will take into account that the exponent in Eq. (6) rapidly tends to zero when both θ and τ increase. It allows us to expand the area of integration over these angles from $-\infty$ to $+\infty$. As a result, in the framework of the discussed approximations we get

$$z^c = \frac{\exp(2\lambda)}{\pi}\int_{-\infty}^{\infty} d\theta d\tau \int_0^{\infty}(1+x)dx \times\left\{\exp\left[-\lambda\left(\frac{3}{2}\tau^2 + \frac{3}{2}(\theta-\tau)^2 + 6x\right)\right]\right\}. \tag{10}$$

The integrals in Eq. (10) can be calculated analytically. Neglecting $1/\lambda$ as compared with unity, we come to

$$z^c = \frac{\exp(2\lambda)}{3\sqrt{3}\lambda^2}. \tag{11}$$

Thus the free energy of the linear chain is estimated as

$$f_n^c = -(n-1)kT\ln z^c = -(n-1)[2\lambda - \ln(3\sqrt{3}\lambda^2)]. \tag{12}$$

Comparing Eqs. (12) with (7), we get the following estimate for the parameter ε^c:

$$\varepsilon^c = \varepsilon^{c0} - \ln(3\sqrt{3}\lambda^2), \quad \lambda \gg 1,$$

$$\varepsilon^{c0} = 2\lambda. \tag{13}$$

It should be stressed that the estimate Eq. (13) is obtained only under assumption that $\lambda \gg 1$ and this estimate is incorrect when $\lambda \sim 1$ or less. However, in the last case neither chains nor other heterogeneous clusters can appear in a ferrofluid.

The right part of Eq. (13) consists of two parts. The first one ε^{c0} corresponds to the ground state of the doublet when all three vectors $\mathbf{m}_{1,2}$ and $\mathbf{r}_{12}$ are parallel. The second term, with the logarithm, appears due to the fluctuations of these vectors and corresponds to the cluster entropy. The logarithm in Eq. (13) is more, the entropy is less.

IV. EFFECTIVE ENERGY ε^t OF THE TRIPLET

Let us consider now a triplet shown in Fig. 4. First of all, we will estimate the ground state of this triplet. It is obvious, from the symmetry of the problem, that the ground state corresponds to disposition of the particles in the form of a regular triangle with size length equal to the particle diameter d_p. The problem is to determine the ground angle θ^0

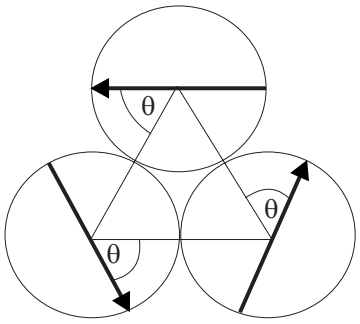

FIG. 4. Sketch of the triplet in the ground state.

between the particle magnetic moment and side of this triangle.

It follows from the symmetry of the problem that the angles θ^0 of all particles must be equal. Taking this into account, we can write the ground energy U^{t0} of the dipole-dipole interaction between particles in the triplet as (see Fig. 4)

$$U^{t0} = -3\lambda kT\left[3\cos\theta^0\cos\left(\frac{\pi}{3}+\theta^0\right)-\cos\left(\frac{2\pi}{3}\right)\right]. \tag{14}$$

The first multiplier 3 takes place here due to the fact that we deal with three bonds between the particles in the triplet.

Minimizing Eq. (14) with respect to θ^0, we have $\theta^0 = \pi/3$.

Now we should estimate the triplet free energy taking into account fluctuations of the particle positions and orientations of their moments as well. As in the previous part, we consider the entirely 2D problem, assuming that particle moments and their positions fluctuate in the plane of the triplet.

The triplet free energy can be presented as

$$f^t = -kT\ln(2Z^t),$$

$$Z^t = \frac{1}{s^2}\int \exp(-U^t)d\mathbf{m}_2 d\mathbf{m}_3 d\mathbf{r}_{12} d\mathbf{r}_{23},$$

$$U^t = u_{12}+u_{23}+u_{31}. \tag{15}$$

The multiplier 2 in the logarithm (15) appears because there are two particle moment orientations in the "tie"—clockwise and in the opposite direction.

As in Sec. III, we estimate the free energy by using the saddle-point method. It means that we suppose the exponent in Eq. (15) to have a sharp maximum in the ground state of this cluster and take into account only small deviations from this state.

Let us introduce a polar coordinate system with the axis aligned along the magnetic moment $\mathbf{m}_1$ of the first particle in the triplet (see Fig. 5). We denote by θ_2 and θ_3 and τ_1, τ_2, and τ_3 the angles between this axis and the moments $\mathbf{m}_2$ and $\mathbf{m}_3$, as well as between this axis and radius vectors $\mathbf{r}_{12}$, $\mathbf{r}_{23}$, and $\mathbf{r}_{31}$, respectively. We also introduce the internal angles α_1, α_2, and α_3 of the triangle shown in Fig. 5. In the ground state of this triplet the following equalities are true:

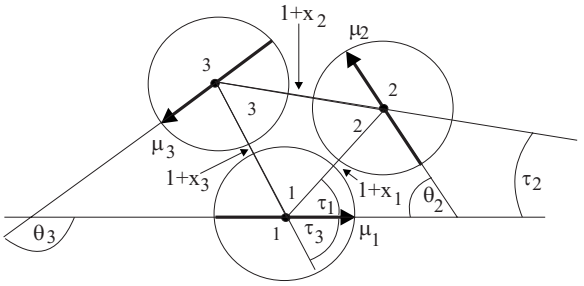

FIG. 5. Illustration of the triplet free energy calculations—polar angles and dimensionless distances between the particles.

$$t_1^0 = \frac{\pi}{3}, \quad \tau_2^0 = \pi, \quad \tau_3^0 = -\frac{\pi}{3},$$

$$\theta_2^0 = \frac{2\pi}{3}, \quad \theta_3^0 = -\frac{2\pi}{3}, \quad |\mathbf{r}_{ij}^0| = d, \quad \alpha_i^0 = \frac{\pi}{3}. \tag{16}$$

Here and below the upper index 0 marks the magnitudes corresponding to the ground state of a cluster. Let us introduce the deviations of these magnitudes from their ground values:

$$\delta\tau_i = \tau_i - \tau_i^0, \quad \delta\theta_i = \theta_i - \theta_i^0, \quad \delta\alpha_i = \alpha_i - \alpha_i^0,$$

$$x_1 = \frac{|\mathbf{r}_{12}|}{d_p} - 1, \quad x_2 = \frac{|\mathbf{r}_{23}|}{d_p} - 1, \quad x_3 = \frac{|\mathbf{r}_{31}|}{d_p} - 1. \tag{17}$$

We assume that the absolute magnitudes of these deviations are much less than unity. Indeed, only in the case of small fluctuations can we consider the particles in the triplet as bounded. In the linear approximation with respect to x_i the dimensionless energy of the dipole interaction in the triplet can be written as

$$\begin{aligned} U^t = -\lambda\Big[&3\cos\tau_1\cos(\tau_1-\theta_2)-\cos\theta_2+3\cos(\theta_2-\tau_2)\\ &\times\cos(\tau_2-\theta_3)-\cos(\theta_2-\theta_3)+3\\ &\times\cos(\theta_3-\tau_3)\cos\tau_3-\cos\theta_3-3\left(\cos^2\frac{\pi}{3}-\cos\frac{2\pi}{3}\right)\\ &\times(x_1+x_2+x_3)\Big]. \end{aligned} \tag{18}$$

By using the notation in Eq (17) and taking into account Eq. (16) in the main approximation with respect to $\delta\theta_i$ and $\delta\tau_i$ one can rewrite Eq. (18) in the following form:

$$\begin{aligned} U^t = -\frac{15}{4}\lambda + \lambda\Big[&\frac{9}{4}\delta\tau_1(\delta\tau_1-\delta\theta_2)+\frac{3}{8}\delta\tau_1^2+\frac{3}{8}(\delta\tau_1-\delta\theta_2)^2\\ &+\frac{1}{4}\delta\theta_2^2+\frac{9}{4}(\delta\tau_2-\delta\theta_2)(\delta\tau_2-\delta\theta_3)+\frac{3}{8}(\delta\tau_2-\delta\theta_2)^2\\ &+\frac{3}{8}(\delta\tau_2-\delta\theta_3)^2+\frac{1}{4}(\delta\theta_2-\delta\theta_3)^2+\frac{9}{4}\delta\tau_3(\delta\tau_3-\delta\theta_3) \end{aligned}$$

$$+\frac{3}{8}\delta\tau_3^2+\frac{3}{8}(\delta\tau_3-\delta\theta_3)^2+\frac{1}{4}\delta\theta_3^2+\frac{15}{4}(x_1+x_2+x_3)\Bigg]. \tag{19}$$

By using simple geometrical considerations (see Fig. 5) one can obtain the following relations between angles α_i and τ_i:

$$\alpha_1=\tau_3-\tau_1,\quad \alpha_2=\tau_2-\tau_3,\quad \alpha_3=\pi+\tau_1-\tau_2.$$

Therefore

$$\delta\alpha_1=\delta\tau_3-\delta\tau_1,\quad \delta\alpha_2=\delta\tau_2-\delta\tau_3,\quad \delta\alpha_3=\delta\tau_1-\delta\tau_2. \tag{20}$$

Integrating in Eq. (15) over $\mathbf{r}_{12}$ and $\mathbf{r}_{23}$, we can consider x_1, x_2, $\delta\alpha_2$, and τ_1 as independent variables. Our aim now is to express τ_2, τ_3, and x_3 in terms of x_1, x_2, $\delta\alpha_2$, and τ_1.

The well-known cosine theorem gives

$$(1+x_3)^2=(1+x_1)^2+(1+x_2)^2-(1+x_1)(1+x_2)\cos\alpha_2. \tag{21}$$

Taking into account that

$$\cos\alpha_2=\cos\left(\frac{\pi}{3}+\delta\alpha_2\right)\approx\frac{1}{2}-\frac{\sqrt{3}}{2}\delta\alpha_2$$

in the linear approximation with respect to x_i and $\delta\alpha_2$ we get from Eq. (21)

$$x_3=\frac{x_1+x_2}{2}+\frac{\sqrt{3}}{2}\delta\alpha_2. \tag{22}$$

The well-known theorem of sines gives

$$\frac{\sin\alpha_3}{1+x_1}=\frac{\sin\alpha_2}{1+x_3}=\frac{\sin\alpha_1}{1+x_2}.$$

In the linear approximation it leads to

$$\delta\alpha_1=-\frac{1}{2}\delta\alpha_2+\frac{\sqrt{3}}{2}(x_1+x_2). \tag{23}$$

By using the relation in Eq. (20), we get from here

$$\delta\tau_3=-\frac{1}{2}\delta\alpha_2+\frac{\sqrt{3}}{2}(x_2-x_1)+\delta\tau_1, \tag{24}$$

$$\delta\tau_2=\delta\tau_1-\delta\alpha_2.$$

Substituting Eq. (24) into Eq. (19), in the linear approximation with respect to $\delta\alpha$, x_1, and x_2 we have

$$U^t=-\frac{15}{4}\lambda+\lambda\Bigg[\frac{9}{4}\delta\tau_1(\delta\tau_1-\delta\theta_2)+\frac{3}{8}\delta\tau_1^2+\frac{3}{8}(\delta\tau_1-\delta\theta_2)^2+\frac{1}{4}\delta\theta_2^2+\frac{9}{4}(\delta\tau_1-\delta\theta_2)(\delta\tau_1-\delta\theta_3)+\frac{3}{8}(\delta\tau_1-\theta_2)^2+\frac{3}{8}(\delta\tau_1-\delta\theta_3)^2$$
$$+\frac{1}{4}(\delta\theta_2-\theta_3)^2+\frac{9}{4}\delta\tau_1(\delta\tau_1-\delta\theta_3)+\frac{3}{8}\delta\tau_1^2+\frac{3}{8}(\delta\tau_1-\delta\theta_3)^2+\frac{1}{4}\delta\theta_2^2+\frac{15}{4}\left(\frac{3}{2}(x_1+x_2)+\frac{\sqrt{3}}{2}\delta\alpha_2\right)\Bigg]. \tag{25}$$

By using the saddle-point approximation, we can write down the statistical integral in (16) as

$$Z^t=\frac{1}{\pi^2}\int_{-\infty}^{\infty}d\delta\theta_2 d\delta\theta_3 d\tau_1\int_0^{\infty}dx_1dx_2$$
$$\times\int_{-\sqrt{3}(x_1+x_2)}^{\infty}d\delta\alpha_2[\exp(-U^t)]. \tag{26}$$

Substituting here Eq. (25), we can calculate the integrals on $\delta\alpha_2$, x_1, and x_2 analytically. The integrals on $\delta\theta_i$ and $\delta\tau_2$ can be calculated numerically. As a result, taking into account that only the case $\lambda\gg 1$ is considered and neglecting λ^{-1} as compared with 1, we get

$$Z^t=\frac{\exp(15\lambda/4)}{\lambda^{9/2}\pi^{1/2}}1.54\left(\frac{4}{15}\right)^3\frac{2}{\sqrt{3}}\approx\frac{\exp(15\lambda/4)}{\lambda^{9/2}\pi^{1/2}}0.034. \tag{27}$$

Combining Eq. (27) with the first expression in (15), we come to the following estimate for the own free energy of the triplet:

$$\varepsilon^t=\varepsilon^{t0}-\ln\left(2\frac{\pi^{1/2}\lambda^{9/2}}{0.034}\right),$$

$$\varepsilon^{t0}=\frac{15}{4}\lambda. \tag{28}$$

It should be stressed that the estimate in Eq. (28), like Eq. (13), has been obtained only for the case $\lambda\gg 1$. This result can not be used when $\lambda\sim 1$ or less. Moreover, for the case $\lambda=1$ it leads to the nonphysical result $\varepsilon<0$, which is an artifact of the saddle-point approximation. It has been already noted that in the case $\lambda=1$ the chains and other aggregates cannot exist; that is why this case is beyond our interest here.

Like expression in Eq. (13), the estimate in Eq. (28) consists of two parts. The first one ε^{t0} corresponds to the ground state of the triplet. The second one, with logarithm, appears

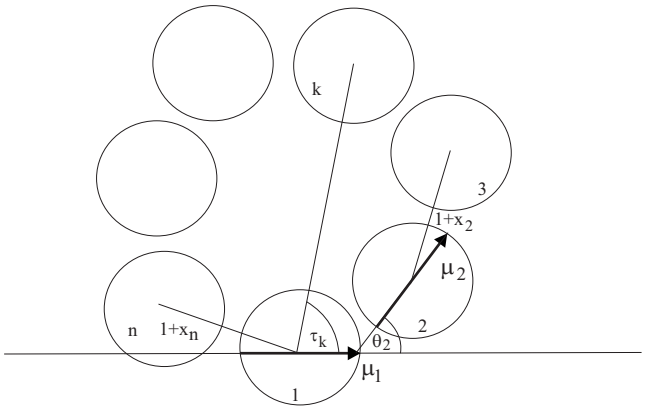

FIG. 6. Sketch of the n-particle ring.

due to fluctuations of the particle positions and orientations of their magnetic moments. This is the entropy part of the triplet free energy. An increase of the logarithm means a decrease of the triplet entropy.

Comparing Eq. (28) with Eq. (13), one can see that the triplet coupling parameter ε^t is less than the total parameter $2\varepsilon^c$ for the chain consisting of three particles. This inequality takes place because of two reasons. First, the triplet ground term ε^{t0} is less than that, $2\varepsilon^c=4\lambda$, for the chain. Second, the logarithmic term in Eq. (28) is significantly more than that in the expression for Eq. (13). This means that the entropy of the triplet is less than the entropy of the three-particle chain. That is why the probability of appearance of the closed triplet must be significantly less than that of the three-particle chain.

The same conclusion can be made for the closed quartet. Calculations, which we omit here, show that the absolute magnitude of the ground part of the quartet free energy is equal to the magnitude of the ground part of the free energy of the four-particle chain, whereas the entropy of the quartet is much less than the entropy of the chain. This means that the probability of appearance of the quartet is significantly less than the same for the four-particle chain. Starting from the five-particle closed ring, the absolute magnitude of the energy of the ground state of the ring is higher than that of the chain with the same number of particles. However, of course, the ring entropy is less than the chain entropy. That is why in Eqs. (1) and (2) we neglect the closed quartets; however, we take into account the rings with five and more particles.

V. EFFECTIVE ENERGY ε^r OF THE RING

Let us consider a ring consisting of n $(n\geqslant 5)$ particles (Fig. 6). By using the same considerations as for the triplet, one can show that the ground state of the ring corresponds to the regular polygon. Magnetic moments of particles in this state deviate from the polygon side at the angle π/n, i.e., in the ground state the moments are perpendicular to the polygon radii. The polygon side in this state equals the particle diameter d. Our aim now is to estimate the ring free energy f_n^r, taking into account fluctuations of positions and orientations of the particles.

This free energy can be estimated as

$$f_n^r = -kTn\varepsilon_n^r = -kT\ln(2Z_n^r), \tag{29}$$

where

$$Z_n^r = \frac{1}{s^{n-1}}\int \exp(-U_n^r)d\mathbf{m}_2\cdots d\mathbf{m}_n d\mathbf{r}_{12}\cdots d\mathbf{r}_{n1},$$

$$U_n^r = u_{12}+u_{23}+\cdots+u_{n-1,n}+u_{n1}. \tag{30}$$

The multiplier 2 appears here, as for the case of the three-particle "tie," due to the fact that there two types of particle moment orientations in the ring—clockwise and the opposite one.

In order to estimate Z_n^r, we introduce a polar coordinate system with the axis aligned along the magnetic moment of the first particle in the ring (see Fig. 8, below).

We denote as $\theta_2,\theta_3,\ldots,\theta_n$ the angles between the moments of the second, third,…, nth particles and the polar axes $\tau_1,\tau_2,\ldots,\tau_n$ the angles between the vectors $\mathbf{r}_{12},\mathbf{r}_{23},\ldots,\mathbf{r}_{n1}$ and the axis, respectively. We introduce also the notation

$$x_1=\frac{|\mathbf{r}_{12}|}{d_p}-1,\quad x_2=\frac{|\mathbf{r}_{23}|}{d_p}-1,\ldots,\quad x_n=\frac{|\mathbf{r}_{n1}|}{d_p}-1 \tag{31}$$

and suppose that the strong inequality $x_i\ll 1$ holds for every i. In other words, we take into account only small fluctuations of the ring from its ground state.

In the linear approximation with respect to x_i, the dimensionless potential energy U_n^r can be estimated as

$$\begin{aligned}U_n^r = -\lambda\Big[&3\cos\tau_1\cos(\tau_1-\theta_2)-\cos\theta_2\\&+3\cos(\tau_2-\theta_2)\cos(\tau_2-\theta_3)-\cos(\theta_3-\theta_2)+\cdots\\&+3\cos(\tau_{n-1}-\theta_{n-1})\cos(\tau_{n-1}-\theta_n)-\cos(\theta_{n-1}-\theta_n)\\&+3\cos\tau_n\\&\times\cos(\tau_n-\theta_n)-\cos\theta_n+\left(9\cos^2\frac{\pi}{n}-3\cos\frac{2\pi}{n}\right)\\&\times(x_1+x_2+\cdots+x_n)\Big].\end{aligned} \tag{32}$$

Let us introduce the deviations of the angles θ_i and τ_i from their ground magnitudes θ_i^0 and τ_i^0 as

$$\delta\theta_i=\theta_i-\theta_i^0,\quad \delta\tau_i=\tau_i-\tau_i^0.$$

The relation

$$\tau_i^0=\frac{\pi}{n}+(i-1)\frac{2\pi}{n}$$

follows from simple geometrical considerations (see Fig. 6).

We suppose that these deviations are also small. In the main approximation with respect to these deviations, the potential in Eq. (32) can be written as

$$U_n^r = -\lambda\Bigg[3\left(\cos^2\frac{\pi}{n} - \sin^2\frac{\pi}{n}\delta\tau_1(\delta\tau_1 - \delta\theta_2) - \frac{1}{2}\cos^2\frac{\pi}{n}\delta\tau_1^2 - \frac{1}{2}\cos^2\frac{\pi}{n}(\delta\tau_1 - \delta\theta_2)^2\right) - \cos\frac{2\pi}{n} + \frac{1}{2}\cos\frac{2\pi}{n}\delta\theta_2^2 + 3\left(\cos^2\frac{\pi}{n}\right.$$
$$\left. - \sin^2\frac{\pi}{n}(\delta\tau_2 - \delta\theta_2)(\delta\tau_2 - \delta\theta_3) - \frac{1}{2}\cos^2\frac{\pi}{n}(\delta\tau_2 - \delta\theta_2)^2 - \frac{1}{2}\cos^2\frac{\pi}{n}(\delta\tau_2 - \delta\theta_3)^2\right) - \cos\frac{2\pi}{n} + \frac{1}{2}\cos\frac{2\pi}{n}(\delta\theta_3 - \delta\theta_2)^2 + \cdots$$
$$+ 3\left(\cos^2\frac{\pi}{n} - \sin^2\frac{\pi}{n}(\delta\tau_{n-1} - \delta\theta_{n-1})(\delta\tau_{n-1} - \delta\theta_n) - \frac{1}{2}\cos^2\frac{\pi}{n}(\delta\tau_{n-1} - \delta\theta_{n-1})^2 - \frac{1}{2}\cos^2\frac{\pi}{n}(\delta\tau_{n-1} - \delta\theta_n)^2\right) - \cos\frac{2\pi}{n}$$
$$+ \frac{1}{2}\cos\frac{2\pi}{n}(\delta\theta_n - \delta\theta_{n-1})^2 + 3\left(\cos^2\frac{\pi}{n} - \sin^2\frac{\pi}{n}\delta\tau_n(\delta\tau_n - \delta\theta_n) - \frac{1}{2}\cos^2\frac{\pi}{n}\delta\tau_n^2 - \frac{1}{2}\cos^2\frac{\pi}{n}(\delta\tau_n - \delta\theta_n)^2\right) - \cos\frac{2\pi}{n}$$
$$+ \frac{1}{2}\cos\frac{2\pi}{n}\delta\theta_n^2 + \left(9\cos^2\frac{\pi}{n} - 3\cos\frac{2\pi}{n}\right)(x_1 + x_2 + \cdots + x_n)\Bigg]. \tag{33}$$

The obvious closure condition of the ring,

$$\mathbf{r}_{n1} = -(\mathbf{r}_{12} + \mathbf{r}_{23} + \cdots + \mathbf{r}_{n-1,n}), \tag{34}$$

does not allow us to consider all variables x_i and $\delta\tau_i$ in Eq. (33) as independent. By using Eq. (34) we can express x_n and $\delta\tau_n$ through the rest variables x_i and $\delta\tau_i$. To this end we can present Eq. (35) as follows:

$$(1 + x_n)\cos(\tau_n^0 + \delta\tau_n) = -\sum_{i=1}^{n-1}(1 + x_i)\cos(\tau_i^0 + \delta\tau_i),$$

$$(1 + x_n)\sin(\tau_n^0 + \delta\tau_n) = -\sum_{i=1}^{n-1}(1 + x_i)\sin(\tau_i^0 + \delta\tau_i).$$

In the linear approximation with respect to x_j and $\delta\tau_j$ we therefore get

$$x_n\cos\tau_n^0 - \delta\tau_n\sin\tau_n^0 = -\sum_{i=1}^{n-1}x_i\cos\tau_i^0 + \sum_{i=1}^{n-1}\delta\tau_i\sin\tau_i^0,$$

$$x_n\sin\tau_n^0 + \delta\tau_n\cos\tau_n^0 = -\sum_{i=1}^{n-1}x_i\sin\tau_i^0 - \sum_{i=1}^{n-1}\delta\tau_i\cos\tau_i^0. \tag{35}$$

Let us introduce new variables $\psi_i = \delta\tau_i - \delta\tau_1$. Taking into account the condition of the ring closedness,

$$\sum_{i=1}^{n}\cos\tau_i^0 = 0, \quad \sum_{i=1}^{n}\sin\tau_i^0 = 0,$$

and by using the new variables ψ_i, one can rewrite in Eq. (35) as

$$x_n\cos\tau_n^0 - \psi_n\sin\tau_n^0 = -A,$$

$$x_n\sin\tau_n^0 + \psi_n\cos\delta\tau_n^0 = -B,$$

$$A = \sum_{i=1}^{n-1}x_i\cos\tau_i^0 - \sum_{i=2}^{n-1}\psi_i\sin\tau_i^0,$$

$$B = \sum_{i=1}^{n-1}x_i\sin\tau_i^0 + \sum_{i=2}^{n-1}\psi_i\cos\tau_i^0. \tag{36}$$

The system in Eq. (36) has the following solutions:

$$x_n = -A\cos\tau_n^0 + B\sin\tau_n^0,$$

$$\psi_n = -B\cos\tau_n^0 + A\sin\tau_n^0. \tag{37}$$

Combining Eqs. (33) and (37), substituting the result into Eq. (30), and taking into account that

$$d\mu_2\cdots d\mu_n d\mathbf{r}_{12}\cdots\mathbf{r}_{n-1,n} = (d_p)^{n-1}d\delta\theta_2\cdots d\delta\theta_n d\psi_2\cdots d\psi_{n-1}dx_1\cdots dx_{n-1},$$

we can calculate the statistical integral Z_n^r.

Let us discuss now the procedure of this integration. Substituting Eq. (37) into Eq. (33), after simple transformations we get the following relation for the potential energy of the ring:

$$U_n^r = -n\varepsilon_n^{r0} + \delta U_{n1}^r + \delta U_{n1}^r, \tag{38}$$

where

$$\varepsilon_n^{r0} = \lambda\left[1 + \cos^2\left(\frac{\pi}{n}\right)\right] \tag{39}$$

and

$$\delta U_{n1}^r = \lambda\Bigg\{\sum_{i=1}^{n}\left[3(\delta\tau_1 + \psi_i)^2 - (\delta\tau_1 + \psi_i)(\delta\theta_i + \delta\theta_{i+1})\right] + \frac{1}{2}\left[1 + \cos^2\left(\frac{\pi}{n}\right)\right](\delta\tau_i^2 + \delta\theta_{i+1}^2) + \left[1 + \sin^2\left(\frac{\pi}{n}\right)\right]\delta\theta_i\delta\theta_{i+1}\Bigg\},$$

$$\psi_1 \equiv \delta\theta_1 \equiv \delta\theta_{n+1} \equiv 0,$$

$$\delta U^r_{n2} = 3\lambda\left[1+\cos^2\left(\frac{\pi}{n}\right)\right](x_1+x_2+\cdots+x_n). \quad (40)$$

Here

$$x_n = \sum_{i=2}^{n-1}\psi_i \sin(\tau_i^0-\tau_n^0) - \sum_{i=1}^{n-1} x_i \cos(\tau_i^0-\tau_n^0),$$

$$\psi_n = -\sum_{i=2}^{n-1}\psi_i \cos(\tau_i^0-\tau_n^0) - \sum_{i=1}^{n-1} x_i \sin(\tau_i^0-\tau_n^0). \quad (41)$$

Analysis shows that the order of integration on variables ψ_j, x_i, and $\delta\theta_k$ does not affect the magnitude of the integral in Eq. (30). For definiteness, first, we will integrate on ψ_2. Integrating on ψ_2, we must provide the obvious condition $x_n > 0$. Thus, in the framework of the saddle-point approximation, the region of integration on ψ_2 should be between the limits

$$\psi_{2\,min} = -\frac{1}{\sin(\tau_2^0-\tau_n^0)} \times\left[\sum_{i=3}^{n-1}\psi_i \sin(\tau_i^0-\tau_n^0) - \sum_{i=1}^{n-1} x_i \cos(\tau_i^0-\tau_n^0)\right] \quad (42)$$

and

$$\psi_{2\,max} = \mathrm{sgn}[\sin(\tau_2^0-\tau_n^0)]\times\infty.$$

Let us consider the integral

$$\int_{\psi_{2\,min}}^{\psi_{2\,max}} \exp\{-\delta U^r_{n1}(\psi_2)\exp[-\delta U^r_{n2}(\psi_2)]d\psi_2\}.$$

For simplification we omit here all arguments of the functions δU_{n1} and δU_{n2} except ψ_2. Since δU_{n2} linearly depends on ψ_2, for large λ when $\psi_2 \to \psi_{2max}$ the function $\exp[-\delta U^r_{n2}(\psi_2)]$ tends to zero much faster than $\exp[-\delta U^r_{n2}(\psi_2)]$. Thus, in the saddle-point approximation, we can estimate the last integral as

$$\int_{\psi_{2\,min}}^{\psi_{2\,max}} \exp[-\delta U^r_{n1}(\psi_2)]\exp[-\delta U^r_{n2}(\psi_2)]d\psi_2 \approx \exp[-\delta U^r_{n1}(\psi_{2\,min})]\int_{\psi_{2\,min}}^{\psi_{2\,max}} \exp[-\delta U^r_{n2}(\psi_2)]d\psi_2$$
$$= \frac{\exp[-\delta U^r_{n1}(\psi_{2\,min})]}{3\lambda\left(1+\cos^2\frac{\pi}{n}\right)|\sin(\tau_i^0-\tau_n^0)|}\exp\left[-3\lambda\left(1+\cos^2\frac{\pi}{n}\right)(x_1+\cdots+x_{n-1})\right]. \quad (43)$$

Therefore in the framework of this approximation we have

$$Z^r_n = \frac{1}{\pi^{n-1}}\frac{\exp(n\varepsilon_n^{r0})}{3\lambda\left(1+\cos^2\frac{\pi}{n}\right)|\sin(\tau_i^0-\tau_n^0)|} \times\int \exp(-\delta U^r_{n1})\exp\left[-3\lambda\left(1+\cos^2\frac{\pi}{n}\right)(x_1+\cdots+x_{n-1})\right]d\delta\theta_2\cdots d\delta\theta_n d\delta\tau_1 d\psi_3\cdots d\psi_{n-1}dx_1\cdots dx_{n-1},$$

$$\delta U^r_{n1} = \delta U^r_{n1}(\delta\tau_1, \psi_{2\,min}, \psi_3, \ldots, \psi_{n-1}, \psi_n, \delta\theta_2, \ldots, \delta\theta_n), \quad (44)$$

where ψ_{2min} and ψ_n as functions of $\psi_3,\ldots,\psi_{n-1}$ and $x_1,\ldots,x_{n-1}$ are determined in Eqs. (42) and (37), respectively.

With respect to $x_1,\ldots,x_{n-1}$ we should integrate between 0 and ∞. Due to the fact that the second exponent in the integral in Eq. (44) linearly depends on $x_1,\ldots,x_{n-1}$, whereas δU_{n2} is a nonlinear function of ψ_{2min}, $\psi_3,\ldots,\psi_{n-1}$, in the case $\lambda \gg 1$ the second exponent in (44) tends to zero with increasing $x_1,\ldots,x_{n-1}$ much faster than the first one. Therefore, in the framework of the the saddle-point approximation, we get

$$\int \exp(-\delta U^r_{n1})\exp\left[-3\lambda\left(1+\cos^2\frac{\pi}{n}\right)\times(x_1+\cdots+x_{n-1})\right] \times d\delta\theta_2\cdots d\delta\theta_n d\delta\tau_1 d\psi_3\cdots d\psi_{n-1}dx_1\cdots dx_{n-1}$$
$$\approx \exp(-\delta U^r_{n1}|_{x_1=\cdots=x_{n-1}=0}) \times\int_0^\infty \exp\left[-3\lambda\left(1+\cos^2\frac{\pi}{n}\right)\times(x_1+\cdots+x_{n-1})\right]d\delta\theta_2\cdots d\delta\theta_n d\delta\tau_1 d\psi_3\cdots \times d\psi_{n-1}dx_1\cdots dx_{n-1}.$$

By using this estimate in Eq. (44), we come to the following relation:

$$Z^r_n = \frac{1}{\pi^{1/2}}\frac{\exp(\varepsilon_n^{r0})}{3\lambda\left(1+\cos^2\frac{\pi}{n}\right)|\sin(\tau_i^0-\tau_n^0)|}L_n G_n, \quad (45)$$

where

$$L_n = \int_0^\infty \exp\left[-3\lambda\left(1+\cos^2\frac{\pi}{n}\right)\times(x_1+\cdots+x_{n-1})\right]dx_1\cdots dx_{n-1} = \frac{1}{\left[3\lambda\left(1+\cos^2\frac{\pi}{n}\right)\right]^{n-1}} \quad (46)$$

and

TABLE I. Calculated magnitudes of K_n vs the number n particles in the ring.

n	5	6	7	8	9	10	11	12
K_n	0.17	0.125	0.082	0.055	0.037	0.037	0.0207	0.015

$$G_n = \pi^{-(2n-3)/2} \int_{-\infty}^{\infty} \exp(-\delta U_{n1}^r|_{x_1=\cdots=x_{n-1}=0}) \times d\delta\tau_1 d\psi_3 \cdots d\psi_{n-1} d\delta\theta_2 \cdots d\delta\theta_n,$$

$$U_{n1}^r|_{x_1=\cdots=x_{n-1}=0} = \delta U_{n1}^r(\Psi_2, \psi_3, \ldots, \psi_{n-1}, \Psi_n, \delta\theta_2, \ldots, \delta\theta_n). \tag{47}$$

Here

$$\Psi_2 = \psi_{2\,min}|_{x_1=\cdots=x_{n-1}=0} = -\frac{1}{\sin(\tau_2^0 - \tau_n^0)} \sum_{i=3}^{n-1} \psi_1 \sin(\tau_i^0 - \tau_n^0),$$

$$\Psi_n = \psi_n|_{\psi_2=\Psi_2, x_1=\cdots=x_{n-1}=0} = \frac{1}{\sin(\tau_2^0 - \tau_n^0)} \sum_{i=3}^{n-1} \psi_1 \sin(\tau_i^0 - \tau_2^0). \tag{48}$$

The multiplier $\pi^{-(2n-3)/2}$ is introduced in Eq. (47) for convenience.

Combining Eq. (40) with Eqs. (47) and (48), we come to the following relation:

$$\delta U_{n1}^r = \lambda[u_1 + u_2 + \cdots + u_i + \cdots + u_n], \tag{49}$$

where

$$u_1 = 3(\delta\tau_1^2 - \delta\tau_1\delta\theta_2) + \frac{1}{2}\left(1 + \cos^2\frac{\pi}{n}\right)\delta\theta_2^2,$$

$$u_2 = 3[(\delta\tau_1 + \Psi_2)^2 - (\delta\tau_1 + \Psi_2)(\delta\theta_2 + \delta\theta_3)] + \frac{1}{2}\left(1 + \cos^2\frac{\pi}{n}\right) \times (\delta\theta_2^2 + \delta\theta_3^2) + \left(1 + \sin^2\frac{\pi}{n}\right)\delta\theta_2\delta\theta_3,$$

$$\cdots$$

$$u_i = 3[(\delta\tau_1 + \psi_i)^2 - (\delta\tau_1 + \psi_i)(\delta\theta_i + \delta\theta_{i+1})] + \frac{1}{2}\left(1 + \cos^2\frac{\pi}{n}\right) \times (\delta\theta_i^2 + \delta\theta_{i+1}^2) + \left(1 + \sin^2\frac{\pi}{n}\right)\delta\theta_i\delta\theta_{i+1},$$

$$\cdots$$

$$u_n = 3[(\delta\tau_1 + \Psi_n)^2 - (\delta\tau_1 + \Psi_n)\delta\theta_n] + \frac{1}{2}\left(1 + \cos^2\frac{\pi}{n}\right)\delta\theta_n^2. \tag{50}$$

It is convenient to introduce new variables of integration:

$$\tau' = \sqrt{\lambda}\,\delta\tau_1, \quad \theta_i' = \sqrt{\lambda}\,\delta\theta_i, \quad \psi_i' = \sqrt{\lambda}\,\psi_i.$$

By using these variables, we can rewrite (47) as

$$G_n = \lambda^{-(2n-3)/2} K_n,$$

$$K_n = \pi^{-(2n-3)/2} \int_{-\infty}^{\infty} \exp[-(u_1 + \cdots + u_n)] d\tau' d\psi_3' \cdots d\psi_{n-1}' d\theta_2' \cdots d\theta_n', \tag{51}$$

where u_k are the same functions as in Eq. (50) with τ', ψ_i', and θ_i' instead of $\delta\tau_1$, ψ_i, and $\delta\theta_i$, respectively.

The integral in Eq. (51) can be calculated analytically. However, the results are very cumbersome and the size of the formula increases fast with number n. We have calculated K_n by using the symbolic integration in the package MATCAD 2001. Some results of calculations are given in Table I.

Combining Eq. (51) with Eq. (45) and, then, with Eqs. (29) and (30), we get

$$\varepsilon_n^r = \varepsilon_n^{r0} - \frac{1}{n} \ln \frac{\pi^{1/2}\left[3\left(1 + \cos^2\frac{\pi}{n}\right)\right]^n \lambda^{(4n-3)/2}|\sin(\tau_2^0 - \tau_n^0)|}{K_n} - \ln 2. \tag{52}$$

Here ε_n^{r0} is determined in Eq. (39) and

$$\tau_2^0 - \tau_n^0 = \frac{2\pi}{n}(1 - n).$$

The dimensionless coupling parameter ε_n^r, like the chain and tie parameters ε^c and ε^t, consists of two parts. The first one, ε_n^{r0}, corresponds to the ground state of the ring when it has the shape of a regular polygon with particle magnetic moments perpendicular to the polygon radii. The second, logarithmic, term appears due to fluctuations of the polygon shape and particle moments. This term corresponds to the ring entropy. The larger the magnitude of the logarithm, the smaller the entropy.

VI. RESULTS AND DISCUSSION

Some results of the calculations of the absolute magnitude of the ground-state dimensionless energies $(n-1)\varepsilon^{c0}$ and $n\varepsilon_n^{r0}$ of the n-particle chain and ring are shown in Fig. 7. Since $n\varepsilon_n^{r0}$ is more than $(n-1)\varepsilon^{c0}$, the ring ground state is more thermodynamically advantageous than the chain ground state. However, the ring entropy is much less than the entropy of the chain. The absolute magnitudes $(n-1)\varepsilon^c$ and $n\varepsilon_n^r$ of the chain and ring dimensionless free energies, calculated from Eqs. (14) and (53) with account of the entropic logarithmic terms, are shown in Fig. 8. The results show that

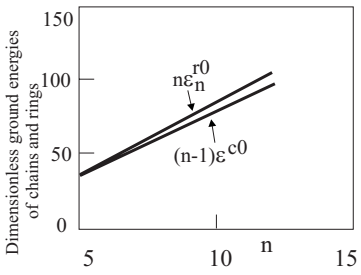

FIG. 7. Absolute magnitudes of dimensionless energies of the chain and ring ground states vs number n of particles in the clusters. $\lambda=4.5$.

for realistic magnitudes of λ the inequality $(n-1)\varepsilon^c > n\varepsilon_n^r$ holds. Therefore, for these magnitudes of λ, the chain state of n-particle clusters is more preferable than the ring state, in spite of the opposite situation with the ground states of these clusters.

Substituting the magnitudes of ε^c, ε^t, and ε_n^r, estimated in Eqs. (13), (28), and (52), into Eq. (3), and by using the normalization condition in Eq. (2), we can calculate the Lagrangian multiplier Λ and, therefore, determine the distribution functions g_n^c, g_n^r, and g_{ijk}^n. It is convenient to take into account the fact that the last function depends only on the total number $n=i+j+k$ of particles in the Y cluster and the relation

$$\sum_{i=1}^{n-2}\sum_{j=1}^{i}\sum_{k=1}^{j} \to \frac{1}{6}[(n-1)^3+1-n]$$

is true. Thus we can introduce the function g_n^Y which is a total concentration of n-particle Y clusters with any distribution of the particles over the cluster branches. It is easy to obtain

$$g_n^Y = \sum_{i=1}^{n-2}\sum_{j=1}^{i}\sum_{k=1}^{j} g_{ijk}^Y = \frac{1}{6s}[(n-1)^3+1-n] \times \exp[\varepsilon^c(n-3)+\varepsilon^t+\Lambda n]. \quad (53)$$

By using Eq. (53), one can transform the last term in the left part of Eq. (2) as

$$\sum_{i\geq j\geq k=1}^{\infty}(i+j+k)g_{ijk}^Y = \sum_{n=3}^{\infty} n g_n^Y.$$

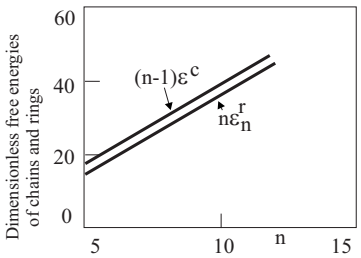

FIG. 8. Absolute magnitudes of dimensionless free energies of the chain and ring vs number n of particles in the clusters. $\lambda=4.5$.

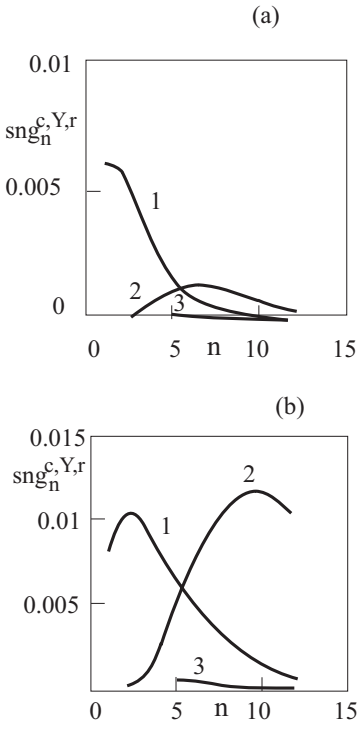

FIG. 9. Volume concentrations of the particles united into the chains (1), into the Y clusters (2), and into the rings (3) when $\lambda=4.5$. The particle surface concentration Φ in the ferrofluid is 0.03 (a) and 0.14 (b).

This form of the term is more convenient for solving Eq. (2) if we are interested in the function g_n^Y, not in the more detailed function g_{ijk}^Y.

Some results of calculations of the surface concentrations ng_n^c, ng_n^Y, and ng_n^r of the particles united into the chains, Y clusters, and in the rings are shown in Fig. 9. These results demonstrate that for the realistic magnitudes of the particle concentration Φ and the parameter λ the majority of particles in the ferrofluid monolayer must be collected in the chains (including single particles) and in the branched clusters. The number of particles in the rings is relatively small. Figure 10 demonstrates the results of our calculations [Eq. (4)] as well as measurements of Ref. [6] of the probabilities p_i that an arbitrary particle has i nearest neighbors. Qualitatively the

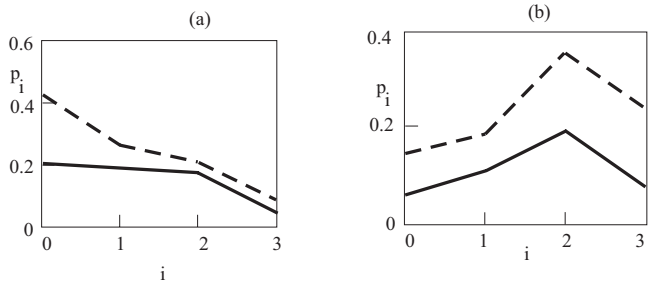

FIG. 10. Probabilities p_i that a particle of the monolayer has i nearest-neighbor particles. Solid lines: calculations. Dashed lines: experiments of [6]. $\lambda=4.5$, and the particle surface concentration Φ in the ferrofluid is 0.03 (a) and 0.14 (b).

theoretical and experimental results are quite similar. Some quantitative difference can be explained by the following approximations of the model. First, we ignore the vertical freedom degree for the particle magnetic moment. This simplification allows us to obtain an analytical expression for the ring free energy; however, it leads to some overestimates of the parameters $\varepsilon^{c,t,r}$ for all types of clusters. Second, we ignore all types of branched clusters except the Y ones. Next, we use the saddle-point approximation. The use of these simplifications has allowed us to obtain the results in a relatively simple form. Generalization of the model to more realistic, however much more complicated from the mathematical viewpoint, situations can be considered as a continuation of this work.

VII. CONCLUSION

We propose a model of equilibrium internal structures in two-dimensional ferrofluid for the case of zero external field. For maximal simplification of calculations, we consider the three simplest types of microstructures: linear chains, Y-like branched clusters, and closed rings. Our analysis shows that for realistic magnitudes of particle concentration and parameter of the dipole-dipole interaction between them, the majority of particles must belong to linear and branched clusters. The number of particles in the rings is relatively small due to the loss of entropy when the particles form the ring. The results of the model are in reasonable agreement with the experiments of [6]. We would like to note that the approximation of the particle moment fluctuating only in the monolayer plane has been used only for a simplification of calculations of the parameters $\varepsilon^{c,t,r}$. Analysis shows that in the framework of the saddle-point approximation the parameters ε^c and ε^t can be estimated taking into account all physically possible orientations of the particle moments—i.e., in both the direction of the plane and perpendicular to that. However, calculation of the ring parameter ε^r presents a significant problem; integrals similar to K_n in Eq. (51) converge too slow. Approximation of the plane fluctuations of the particle moments overestimates parameters $\varepsilon^{c,t,r}$ however can not lead to qualitative change of the main results of our work.

It should be noted that models of the ferrofluid layers with heterogeneous structures and without them has been proposed recently in Refs. [10,11]. The analytical part of Ref. [10] is based on a model of very long polymer macromolecules with bloblike structure and effects of self-avoiding. Computer simulations of this work also demonstrate very long chains. However, the chains and other clusters, detected in real experiments, are quite short. The blob structure of the chains has never been observed experimentally. Our model does not consider effects which dominate in the case of very long chains, but do not play any part in the case of short chains and other clusters, observed in experiments. We have to admit that our results are in quantitative disagreement with the computer simulations of Ref. [10]. In part, first, we have not obtained maxima of the distribution functions over the number of particles in the chains, which have been detected in simulations in Ref. [10]. However, these maxima have not been observed in real experiments in Ref. [6]. The second disagreement between our model and the results of Ref. [10] is in the fact that our calculations, in agreement with experiments in Ref. [6] and other computer simulations (see, for example, Refs. [9,12] and references therein), demonstrate a fast decrease of the distribution functions g_n with the number n of particles in the cluster. In contrast, in the simulations in Ref. [10] the decay of the distribution function is very slow. For example, the magnitudes of the distribution function, corresponding to hundreds of particles in a cluster, are quite comparable with those for single particles. However, long chains, consisting of the hundreds of particles, have never been observed either in real experiments or in other computer simulations. Third, according to simulations in Ref. [10], the concentration of rings in the layer is more than the concentration of the chains and Y-like forks. In our calculations, as in experiments in Ref. [6], the concentration of the rings is definitely less than the concentration of chains and forks. Possibly, the last result can be explained by the fact that we use magnitudes of λ the same as in Ref. [6] which are about twice less than those in the simulations in Ref. [10]. However, the chosen region of magnitudes of λ corresponds to the real modern ferrofluids used in experiments.

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