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TOROID SUSCEPTIBILITY OF AGGREGATED MAGNETIC FLUIDS

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Ferromagnetic suspensions (or magnetic fluids) are complex colloidal systems which are composed of fine magnetic particles uniformly dispersed throughout the carrier liquid [1-3]. In order to prevent the aggregation of colloidal particles some surface-acting agent is used which forms the stabilizing coat on the particle surface. The suspended magnetic particles are almost spherical in form and their sizes are usually close the single-domain value which is about 10...15 nm for the most of the ferromagnetic materials. The magnetic moment of a suspended particle is about $10^4 \dots 10^5$ of Bohr magnetons. Typical magnetic fluid contains magnetite Fe_3O_4 particles which are suspended in kerosene (or diaster) with oleic acid as a surfactant. The thickness of the surfactant layer on the particle surface is about 2...4 nm. Magnetic fluids can considerably vary in their properties according to the type of a surfactant used and the thickness of a layer it forms on the particle surface; their properties also depend on the particle sizes and the kind of ferromagnetic material used to prepare them and so on. For the last time the stable magnetic suspensions are prepared with the particle number concentration till $N \sim 10^{18} 1/cm^3$.These liquids are successfully used in commercial devices such as computer discs, separators of minerals and others.

Most of the properties of magnetic suspensions are explained in terms of the model of noninteracting Brownian particles, having "frozen-in" magnetic moments (it means that the magnetic moment of the particle is rigidly connected with its body) [1-3]. In this case, the dependence of the fluid magnetization on the applied magnetic field H and temperature T is determined by the Langevin function as follows

$$\vec{M} = \mu_0 N \mathcal{L}(\xi) \frac{\vec{H}}{H}; \qquad \mathcal{L}(\xi) = cth(\xi) - \frac{1}{\xi}, \tag{1.1}$$

where N is the particle number density, μ_0 is the value of magnetic moment of an individual particle. The Langevin function argument ξ is a dimensionless parameter which is equal to the ratio of magnetic and thermal energy of a particle : $\xi = \mu_0 H/kT$. But this model cannot explain the properties of the magnetic suspension when the interactions between particles become considerble. The discrepancy between the Langevin behavior and observed phenomena takes place not only in magnetic properties but also in optical and rheological ones [4-9]. The most important effect of the particle interaction is the aggregate formation [1-14]. The theory of a magnetic suspension with aggregate particles was first considered by de Gennes and Pincus [14] and then by other authors (see for example the review articles [10, 11] and also original papers [15-17]). The direct evidence of the existence of the magnetic particle aggregates in stable ferromagnetic fluids has recently been given by small angle neutron scattering technique [17].

It follows from this treatment that in dilute suspension (i.e. at low particle density) in the absence of external magnetic field only small aggregates are present. The number of particles in such an aggregate is less than 10. But when the particle density increases the aggregate sizes grow as well. Thus, they can form fractal clusters, network structures, 'domain' and so on. Here, only small aggregates will be considered as they usually exist in stable suspensions.

When the aggregates are sufficiently small in size the suspension of aggregated particles also may be described by the model of noninteracting Brownian particles. But in this case, the suspended 'particles' have more complex structures which, moreover, can be changed under the action of external field and heating. It should be noted that although there are many publications devoted to the aggregated suspension studies, most of them were performed without taking into account the exact aggregate forms and mutual alignments of the magnetic moments of the initial particles inside the aggregate (in the following, initial particles will be called, for convenience, embryones). The main purpose of the present paper is to study the magnetic and spatial configurations of aggregates in magnetic fluids and to investigate their influence on the magnetic properties of a suspension.

In our consideration the initial suspended particles (embryons) are proposed to be uniformly magnetized over their volumes. But it is clear that the aggregate of these particles is not uniformly magnetized. In the state of minimum of magnetic interaction energy the embryons can form closed structures (aggregates) with zero magnetic moments in the zero field. The absence of the total magnetic moment of given ensemble of magnetic dipole particles tells us that other (higher) magnetic multipole moments have to be used for the description of the magnetic configuration of such aggregates. These moments are quadrupole, toroidal and other ones [18-20]. It can be shown (see below) that the main multipole characteristic of the magnetic configurations with closed structures is toroidal moment that has first been introduced into electrodynamics in the paper [18]. It follows that the measurement of toroid polarization of magnetic fluid in external magnetic field and toroid susceptibility together with the usual magnetic measurements can give more precise information about the distribution of magnetic particles in magnetic fluid and especially about the magnetic configurations of aggregates formed .

In the present paper, our consideration is restricted by the model of rigid aggregates ,i.e., it is proposed that aggregates have fixed space configurations. This model is discussed in detail in sect. 2. The algorithms of numerical calculation of magnetic and space configurations of aggregates are described in sect. 3 where also some results of computer simulations are given for rigid aggregates with particle number $n \leq 5$. These results are used in the next sects. of the paper for counting new magnetic characteristic of a suspension - its toroid polarization - as a function of applied magnetic field and temperature. In sect. 4, the treatment is given in the frame of the model of "frosen-in" magnetic dipoles, and in sect. 5, the model of "movable dipoles" is considered.In the last sect. 6, the principal arrangement of an experimental device for measurement of toroid susceptibility is proposed. These measurements are important for practical applications as a new electromagnetic method for controlling the quality of magnetic fluids.

2. Model of rigid aggregates

Aggregation of magnetic particles changes essentially the magnetic properties of a suspension. Let the number density of embryons N be some fixed quantity. It follows from Eq.(1.1) that in the limit of low applied magnetic field H the magnetic polarization of the suspension $\vec{M}$ is equal to

$$\vec{M} = \chi_0 \vec{H}; \qquad \chi_0 = \mu_0^2 N/3kT, \tag{2.1}$$

where the initial magnetic susceptibility of the suspension χ_0 is introduced. We consider a simple example of the susceptibility variation due to the aggregation process. Let us suppose that all embryons in the suspension come to the aggregated state and that all aggregates are composed only of three embryons . In this case, the effective number particle density decreases three times : $N \to N/3$. But the magnetic moment of an aggregate depends on its sort. When the cause of the aggregate formation is magnetic forces, it has the linear (chain) form and the value of its magnetic moment μ is equal to $3\mu_0$, i.e., it increases three times as compared with one embryon. In this case, in accordance with Eq. (2.1) the initial susceptibility would be equal to

$$\chi = (3\mu_0)^2 (\frac{N}{3})/3kT = \mu_0^2 N/kT. \tag{2.2}$$

It follows from this equation that χ is increased three times as regards to the susceptibility of unaggregated particle suspension (embryonic suspension). But when the cause of the aggregate formation is nonmagnetic forces, the aggregate has the form of equilateral triangular (when it is supposed that all embryons are identical) and its summarized magnetic moment would be equal to zero. As a result the magnetic susceptibility of a suspension would also be equal to zero. But in this case the aggregate has toroidal moment (see below Fig.1 and Tab.) and it may be polarized by the vortex magnetic field and the suspension as a whole may be described by new observable quantities - toroid polarization and toroid susceptibility.

The choice of a model of the aggregate depends on the kind of forces predominating in the interaction between the particles. The average energy of an embryon inside the aggregate may be estimated as a sum of four items : the nonmagnetic and magnetic energy of interparticle interactions the values of which are denoted as $\bar{U}$ and $\bar{U}_m$, respectively; the energy of embryon's magnetic dipole in applied magnetic field which is $\mu_0 H$ and the energy of thermal agitation kT. Here, only the model of an aggregate with fixed form is considered, i.e., it is supposed that mutual arrangement of the embryons inside a given aggregate is fixed (the model of rigid aggregates). This model is correct when the energy of nonmagnetic attractive interaction per particle $\bar{U}$ is much larger than the other items of the particle energy :

$$\bar{U} \gg \bar{U}_m; \qquad \bar{U} \gg kT; \qquad \bar{U} \gg \mu_0 H. \tag{2.3}$$

If at the same time the energy $\bar{U}_m$ is much larger than the other two items

$$\bar{U}_m \gg kT; \qquad \bar{U}_m \gg \mu_0 H, \tag{2.4}$$

the mutual alignments of magnetic moments of the embryons can also be considered as fixed ones, i.e., magnetic moments of embryons are "frozen-in" into the aggregate body.

We also consider the model of an aggregate of fixed form but with a "movable" magnetic moments of particles (the model of movable dipoles), i.e., it is supposed here that magnetic dipoles can move under the action of the applied magnetic field. In this case, inequalities (2.3) take place as in the previous case but the inequalities (2.4) (or one of them) have to be changed by approximate equalities : $\bar{U}_m \geq kT$; $\bar{U}_m \sim \mu_0 H$.

Let us shortly discuss other possible models of aggregates. If instead of Eqns. (2.3), (2.4) one supposes that $\bar{U}_m \sim \mu_0 H, \bar{U}_m \sim \bar{U}$, but at the same time $\bar{U} \gg kT$, the thermal agitation would not disintegrate the aggregates but their forms could change under the action of the applied magnetic field. In such a strong magnetic field the compact aggregate transforms into the stretched one, i.e., only chain aggregates would exist in the suspension. The properties of the suspension with these kind of aggregates were studied in detail by other authors [1-11] and therefore we do not consider them here. In addition, the unclosed chain aggregates do not show toroid moments and they are outside our interests from this point of view too. If inequalities (2.3) were changed by the opposite ones the thermal agitation would be sufficiently intensive to disintegrate the aggregates and we would return to the well-known case of an unaggregated suspension.

Now we consider in detail the interaction of the aggregate with nonuniform magnetic field and introduce multipole moments which describe its magnetic configuration. Let n be a number of embryons in a given aggregate, $\vec{m}_a$ and $\vec{r}_a$ be the magnetic moment and the position vector of the embryon having number a $(a = 1, ..., n)$. It is supposed that all moments $\vec{m}_n$ have equal and fixed length, i.e., $|\vec{m}_a| = \mu_0$. The origin of the coordinate system is chosen in the geometric center of the aggregate so that the connection between $\vec{r}_a$ takes place

$$\sum_a \vec{r}_a = 0. \qquad (2.5)$$

The energy of the aggregate of magnetic particles in the nonuniform applied magnetic field is equal to

$$U = -\sum_a (\vec{m}_a \vec{H}(\vec{r}_a)). \qquad (2.6)$$

In practice the length scale of the field space variation L is much larger than the size of the aggregate l considered here. In this case the function $\vec{H}(\vec{r})$ may be expanded into the power series over the center of the aggregate. After that the energy (2.6) can be written in the form

$$U = -(\vec{\mu}\vec{H}) - (\vec{\tau}\vec{G}) - Q_{ik}F_{ik}, \qquad (2.7)$$

where the multipole moments of the aggregate - magnetic $\vec{\mu}$, toroid $\vec{\tau}$ and quadrupole Q_{ik} are introduced

$$\vec{\mu} = \sum_a \vec{m}_a; \quad \vec{\tau} = \frac{1}{2}\sum_a [\vec{r}_a \vec{m}_a]; \quad Q_{ik} = \frac{1}{2}\sum_a (x_{ai} m_{ak} + x_{ak} m_{ai}) - \frac{1}{3}\sum_a (\vec{r}_a \vec{m}_a)\delta_{ik}, \quad (2.8)$$

In Eq.(2.7) the quantities $\vec{H}$, $\vec{G}$ and F_{ik} are respectively the uniform part of the field, which is equal to $\vec{H} = \vec{H}(\vec{r})|_{\vec{r}=0}$, the vortex of the field $\vec{G} = [rot\vec{H}(\vec{r})]_{\vec{r}=0}$ and symmetrical tensor of the field gradient $F_{ik} = [\nabla_i H_k + \nabla_k H_i]_{\vec{r}=0}$. The Maxwell equation $div(\vec{H}) = 0$ was taken into account when deriving Eq.(2.7). As it will be shown below, most of the aggregates have a comparatively small value of quadrupole moments (see Tab.), and therefore, the quadrupole term in Eq. (2.7) will not be considered below . Besides that, the magnetic field induced by the quadrupole moment goes to zero as $1/r^4$; thus, in contrast to the cases of the magnetic and toroidal moments, for macroscopic sample of size L this field decreases as $1/L$ and it is much smaller than the fields of the other two moments.

As it can be seen from expression (2.7), the aggregate of magnetic particles may interact not only with the uniform magnetic field $\vec{H}$ but also with the vortex field. It follows that the connection between the total multipole moments of the suspension - magnetic and toroid ones, denoted by symbols $\vec{M}$ and $\vec{T}$, respectively, and the applied fields $\vec{H}$ and $\vec{G}$ in the linear approximation can be written in the form

$$M_i = \chi^M_{ik} H_k + \chi^{MT}_{ik} G_k; \quad T_i = \chi^{TM}_{ik} H_k + \chi^T_{ik} G_k, \qquad (2.9)$$

where the magnetic χ^M and toroidal χ^T susceptibilities and also the cross susceptibilities χ^{MT} and χ^{TM} are introduced. All these quantities in general are the functions of temperature, the number of embryons and the form of aggregates. Our problem is to find these functions.

3. Numerical simulation of aggregate configuration

To find the magnetic and toroid susceptibilities of an aggregated suspension, one has to know the space form and magnetic configuration of aggregates. If the conditions (2.3) take place, the main cause of the aggregate formation is nonmagnetic forces. The potential energy of these forces can be modelled by the Lennard-Jones interparticle potential [12], as they do in molecular dynamic methods [23] :

$$V = V_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6], \qquad (3.1)$$

where V_0 and r_0 are the parameters determining the depth of the potential (3.1), its minimum and its position. The known methods of the molecular dynamic, [23] was used to find possible space configurations of the aggregates which are shown on Fig.1 for the case when the number of embryons is equal or less than 5. The binding energy of the embryons E is given in Tab. in units of V_0.

Magnetic parameters of aggregates of a given form were found by using the known methods of micromagnetizm [24] which were modified for our case. The energy of magnetic interparticle dipole-dipole interaction can be written in the form

$$U_m = \sum_{a<b} m_{ai} A_{ik}(\vec{r}_{ab}) m_{bk} - \sum m_{ai} D_i(\vec{r}_a), \qquad (3.2)$$

where the notation is introduced

$$A_{ik}(\vec{r}) = (r^2\delta_{ik} - 3x_i x_k)/r^5; \quad D_i(\vec{r}) = H_i + \frac{1}{2}\epsilon_{ikl} G_k x_l, \qquad (3.3)$$

Table . Magnetic parameters of aggregates showing on Fig.1

$n-a$	E/V_0	μ	τ	α	Q	η
3-1	-3	0	1,73	-	0	-
3-2	-2,03	3	0	-	0	-
4-1	-6	0	2	-	0	-
4-2	-5,07	0	2,73	-	0,18	1
4-4	-4,48	0	2,8	-	0	-
4-5	-4,08	3,04	1,39	90	0,32	0,58
4-6	-3,32	1,98	0	-	0,74	0,68
4-7	-3,07	4	0	-	0	-
5-1	-9,10	1,59	2,68	86	0,10	1
5-2	-8,48	1,2	2,86	90	0,55	1
5-3	-8,20	0,7	3,0	130	0,20	1
5-4	-7,18	0,57	3,79	90	0,15	1
5-5	-6,56	4,24	3.87	90	0,93	1
5-6	-6,25	2,12	2,55	90	0,49	0,6
5-7	-6,21	0,013	0	-	0	-
5-8	-6,19	3,11	2,88	60	0,29	1
5-9	-6,16	1,62	2,03	90	0,60	0,15
5-10	-5,56	0	4,21	-	0	-
5-11	-4,10	5	0	-	0	-

The minimum of this energy which is considered as a function of the magnetic moments $\{\vec{m}_a\}$ gives the magnetic configuration of the aggregate. After that the magnetic parameters of aggregates can be found by Eq. (2.8). The procedure of finding the energy minimum is reduced to solving the Landau-Lifshitz equation

$$\dot{\vec{m}}_a = \frac{1}{\lambda}[\vec{m}_a[\vec{m}_a \frac{\partial U}{\partial \vec{m}_a}]], \tag{3.4}$$

where the parameter λ is some effective friction coefficient. The initial magnetic state (which is described by the set of vectors $\vec{m}_a(0)$ at the moment $t=0$) was found by the diagonalization of some matrix (this procedure is given in our work [25]).

Some results of these computations are given in Tab.. The value of the magnetic moment μ_0 of an embryon was taken as a unit for the magnetic moment of the aggregate μ , and the toroidal τ and the quadrupole Q moments are given in Tab. in units of $\mu_0 r_0$. The quadrupole tenzor in the principal coordinate system was

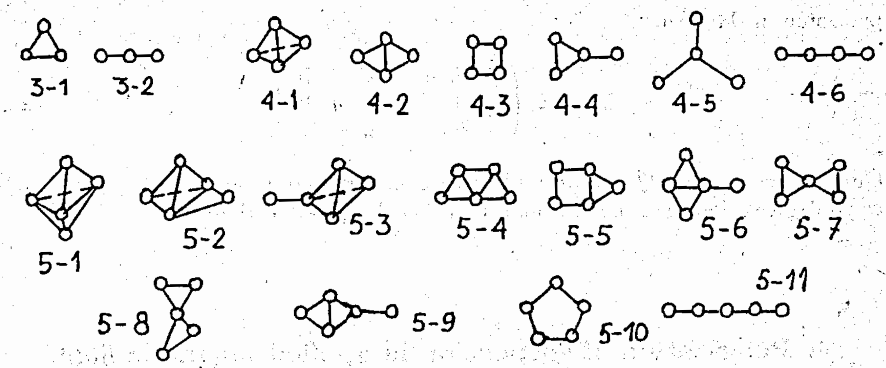

Fig. 1.*The possible forms of "non-magnetic" aggregates with numbers of particles $n \leq 5$. Aggregates (for given n) are numbered by symbols $n-a$ in order of their bonding energy decreasing.*

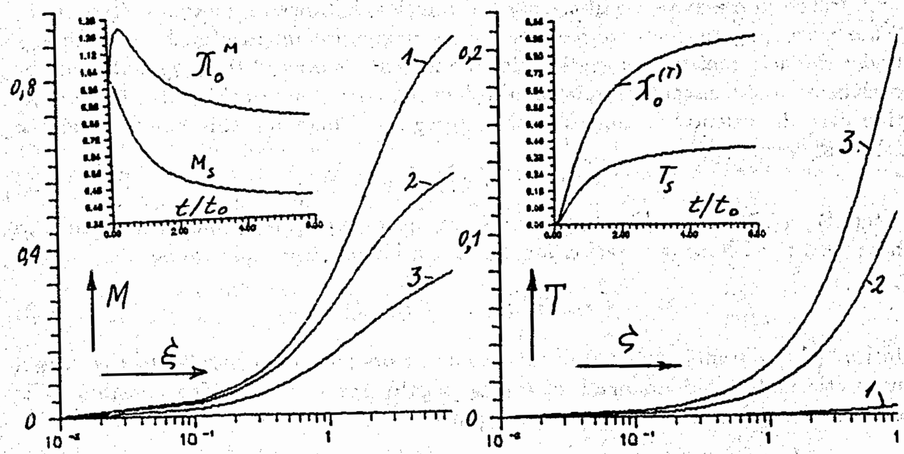

Fig. 2.*Magnetic $\vec{M}$ and toroidal $\vec{T}$ moments of aggregate suspension (for model of "frozen" aggregates) versus non-dimensional applied fields ξ and ζ . The process of particles coagulation is taken into account. The curves 1,2,3 are given for the values of time t/t_0 equal to 0.1, 1 and 5 respectively (here t_0 is a Smoluchovskii time of half coagulated suspension). The dependences of initial magnetic χ_0^M and toroidal χ_0^T susceptibilities on time t/t_0 are shown on the left hand of the figures (a) and (b). On the same figures saturated magnetic ($M_s(t) = limM(\xi,t), \xi \to \infty$) and toroidal ($T_s(t) = limT(\zeta,t), \zeta \to \infty$) moments are shown versus t/t_0. It can be seen from the figures that the magnetic parametres (χ_0^M, M_s) decrease and toroidal ones (χ_0^T, T_s) increase in the course of time.*

presented in the form

$$Q_{ik} = Q\begin{pmatrix} -1+\eta & 0 & 0 \\ 0 & -1-\eta & 0 \\ 0 & 0 & 2 \end{pmatrix}. \qquad (3.5)$$

Quadrupole moment Q and asymmetry parameter η are given in Tab. The angle α (in degrees) between the vectors $\vec{\mu}$ and $\vec{\tau}$ is also given in the table.

4. Polarization of suspension in applied magnetic field. Model of "frozen-in" dipoles

The aggregates suspended in magnetic fluid are in the Brownian motion and therefore the observable quantities have to be calculated by averaging their microscopic analogs with respect to the thermal fluctuation. In the case of rigid aggregates with frozen-in magnetic dipoles, only the rotational Brownian motion is important. Since the aggregate rotates as a whole and its magnetic configuration does not change under the action of the magnetic field, the internal energy of the aggregate may be considered as a constant quantity and it does not contribute to the distribution function over the orientation angles of the aggregate. Therefore, this function has the following form

$$W(\Omega) = Cexp[(\vec{e}\vec{\xi}) + (\vec{n}\vec{\zeta})], \qquad (4.1)$$

where Eq. (2.7) was used for the energy in the exponent (quadrupole term is ommited here) and the following notation for the dimensionless fields is introduced

$$\vec{\xi} = \mu\vec{H}/kT; \qquad \vec{\zeta} = \tau\vec{G}/kT. \qquad (4.2)$$

In Eq. (4.1), symbols $\vec{e}$ and $\vec{n}$ denote unit vectors which are parallel to the known magnetic and toroid moments of the aggregate, respectively. The constant C is determined by the normalization condition

$$\int W(\Omega)d\Omega = 1. \qquad (4.3)$$

Here, the symbol Ω denotes the set of the Eulerian angles θ, φ and ψ. The vectors of the applied fields $\vec{G}$ and $\vec{H}$ are fixed in the laboratory frame of reference, and the vectors $\vec{e}$ and $\vec{n}$ are fixed in the intrinsic frame of the aggregate. Thus, the components of the unit vectors $\vec{n}$ and $\vec{e}$ depend on the Eulerian angles determining the orientation of one frame of reference relative to the other.

The mean values of the densities of the magnetic and toroid moments of suspension are found by using the distribution function in the following way :

$$\vec{M} = N < \vec{\mu} >= \mu N\int \vec{e}W(\Omega)d\Omega; \qquad \vec{T} = N < \vec{\tau} >= \tau N\int \vec{n}W(\Omega)d\Omega. \qquad (4.4)$$

In the case of low field (or what is the same - in the case of high temperatures), when the conditions $\xi \ll 1$, $\zeta \ll 1$ take place, the distribution function is equal to

$$W(\Omega) \cong \frac{1}{8\pi^2}(1 + (\vec{e}\vec{\xi}) + (\vec{n}\vec{\zeta})). \qquad (4.5)$$

Taking into account the values of the integrals

$$\int \vec{e}d\Omega = \int \vec{n}d\Omega = 0; \quad \frac{1}{8\pi^2}\int e_i n_k d\Omega = \frac{1}{3}(\vec{e}\vec{n})\delta_{ik};$$

$$\frac{1}{8\pi^2}\int e_i e_k d\Omega = \frac{1}{8\pi^2}\int n_i n_k d\Omega = \frac{1}{3}\delta_{ik}, \qquad (4.6)$$

it can be found from Eqs. (4.4) and (4.5) that

$$\vec{M} = \frac{1}{3}\mu N(\vec{\xi} + (\vec{e}\vec{n})\vec{\zeta}); \qquad \vec{T} = \frac{1}{3}\tau N(\vec{\zeta} + (\vec{e}\vec{n})\vec{\xi}). \qquad (4.7)$$

Comparing these expressions with Eq. (2.8) the susceptibilities of the suspension can be found (the definition of the fields $\vec{\zeta}$ and $\vec{\xi}$ has to be used for this transformation) :

$$\chi_{ik}^{M} = \frac{\mu^2 N}{3kT}\delta_{ik}; \qquad \chi_{ik}^{T} = \frac{\tau^2 N}{3kT}\delta_{ik}; \qquad \chi_{ik}^{MT} = \chi_{ik}^{TM} = \frac{\tau\mu N}{3kT}(\vec{e}\vec{n})\delta_{ik}. \qquad (4.8)$$

Note that in this approximation the cross susceptibilities are equal to zero when the magnetic and toroid moments of the aggregate are perpendicular to each other.

In the general case, when the fields $\vec{H}$ and $\vec{G}$ are not low and have any mutual orientations, the integrals in Eq.(4.4) may be expressed through the so - called generalized Bessel functions [26]. We do not give here the corresponding cumbersome general expressions and restrict ourselves to some particular cases. When the fields $\vec{H}$ and $\vec{G}$ are the parallel ones, the distribution function (4.1) has the form

$$W(\Omega) = \frac{1}{2\pi\ sh(\xi_0)}exp(\vec{e}_0\vec{\xi}_0), \qquad (4.9)$$

where the vectors $\vec{e}_0$ and $\vec{\xi}_0$ are introduced

$$\vec{e}_0 = \frac{\xi\vec{e} + \zeta\vec{n}}{|\xi\vec{e} + \zeta\vec{n}|}; \qquad \vec{\xi}_0 = \frac{\vec{\xi}\,|\xi\vec{e} + \zeta\vec{n}|}{\xi}. \qquad (4.10)$$

After simple calculations (cf. [27]) the magnetic and toroid moments of the suspension can be found in the form

$$\vec{M} = \mu N(\vec{e}\vec{e}_0)\mathcal{L}(\xi_0)\vec{h}_0; \qquad \vec{T} = \tau N(\vec{n}\vec{e}_0)\mathcal{L}(\xi_0)\vec{h}_0, \qquad (4.11)$$

where $\mathcal{L}(\xi)$ is the Langevin function which is given by Eq. (1.1), $\vec{h}_0$ is a unit vector along the field $\vec{\xi}_0$.

The case, when the magnetic and toroidal moments of the aggregate are parallel to each other ($\vec{n} = \vec{e}$), is also rather simple. The magnetic and toroidal moments of the suspension have the same form as in Eq. (4.11), where yet one has to substitute that

$$\vec{e}_0 = \vec{n} = \vec{e}; \qquad \vec{\xi}_0 = \vec{\xi} + \vec{\zeta}. \tag{4.12}$$

The case when one of the fields $\vec{\xi}$ or $\vec{\zeta}$ is low is also relatively simple.

All formulas derived in the previous calculations take into account only one sort of aggregates. Indeed, in the suspension there are many kinds of aggregates with different number of embryons . The distribution function of the number of embryons in aggregate varies in time (i.e., the suspension turns older). It was shown in sect. 3 that there are several equilibrium forms of aggregates with a given number of embryons which differ from each other in the bonding energy and in the magnetic parametrs (see Fig.1 and Tab.). Let E_{na} be the bonding energy of an aggregate of $a-th$ sort, having n embryons and μ_{na} and τ_{na} be its magnetic and toroidal moments. It follows from the previous treatment that the contribution of aggregates of this sort in the magnetization and toroid moment of the suspension is equal to

$$\vec{M}_{na} = N_{na}\vec{m}(\xi_{na}, \zeta_{na}, \alpha_{na}); \qquad \vec{T}_{na} = N_{na}\vec{t}(\xi_{na}, \zeta_{na}, \alpha_{na}), \tag{4.13}$$

where N_{na} is the number of aggregates of a given sort per unit volume, α_{na} is an angle between the vectors $\vec{e}_{na}$ and $\vec{n}_{na}$. To find average values over the aggregates of different sorts a but with a given particle number n the distribution function can be used

$$N_{na} = \frac{N_n exp\{-E_{na}\beta\}}{\sum_a exp\{-E_{na}\beta\}}, \tag{4.14}$$

where N_n is the particle number density of the aggregates with a given n, β is the quantity reciprocal to kT.

The value N_n depends on time. To find this dependence the Smoluchovski model can be used. This model assumes that the aggregation process is similar to the polymerization chemical reaction $X_1 + X_n = X_{n+1}$ with some given time parameter t_0 (this quantity has the meaning of a time interval when half of the particles have coagulated). The dependence of N_n on time has the form

$$N_n(t) = N_0 \frac{(t/t_0)^{n-1}}{1 + (t/t_0)^{n+1}}, \tag{4.15}$$

where N_0 is the initial density of unaggregated embryons. Putting (4.14),(4.15) into (4.13) the moments $\vec{M}(t)$ and $\vec{T}(t)$ can be avaluated in accounting for distribution of aggregates over their forms and sizes

$$\vec{M}(t) = \sum_{na} \vec{M}_{na}; \qquad \vec{T}(t) = \sum_{na} \vec{T}_{na}. \tag{4.16}$$

These calculations were made numerically taking into consideration all aggregates given in the Tab. Figure 2 shows the magnetization of the suspension and its toroid moment versus the fields ξ and ζ respectively for different time moments. It is clear from Fig. 2 that the saturation magnetization decreases in time and the saturated toroid moment increases. Since in the initial stage mainly two-particle aggregates are formed in the suspension, the susceptibility curve χ_0^M has the hump.

5. Model of movable dipoles

In the previous section, we have considered the model when the magnetic moments of embryons are frozen-in into the aggregate body. In this case, the influence of the applied fields on the Brownian rotational diffusion of aggregates is maximal. The other limiting case takes place when the magnetic moments of embryons are not connected with each other and may be independently oriented by the applied fields (the limit of superparamagnetic aggregates). In this case, the magnetic field does not influence the rotational Brownian diffusion at all and it is impossible to investigate the aggregative structure of suspension by means of the magnetic measurements. This latter case is not interesting for us because it is equivalent to the case of independent particles.

Here, we consider the immediate case when the magnetic moments of embryons can move under the action of the applied field and at the same time interract with each other. To find the average values of moments, one has to use the distribution function of the form

$$dW(\vec{m}_1, ..., \vec{m}_n, \Omega) = C\ exp\{-U(\vec{m}_1, ..., \vec{m}_n, \Omega)\} d\vec{m}_1 ... d\vec{m}_n d\Omega, \tag{5.1}$$

where $-U(\vec{m}_1, ..., \vec{m}_n, \Omega)$ is the magnetic interaction energy of the embryons with each other and with external fields. Integrating over the vectors $\vec{m}_a$ one has to take into account that these vectors have the fixed length. The utilization of such a complicated distribution function is rather difficult for analytical culculations and for numerical computations and therefore some approximate methods have to be used.

When the intrinsic fields on the magnetic moments of embryons are much larger than the applied fields, the alterations of the moments are rather small and they can be taken into account with the aid of magnetic and toroid polarizabilities of the aggregate in consideration. These quantities are introduced in accordance with the equations

$$\mu_i = \mu_i^0 + \kappa_{ik}^m H_k + \kappa_{ik}^{m\tau} G_k; \qquad \tau_i = \tau_i^0 + \kappa_{ik}^{\tau m} H_k + \kappa_{ik}^{\tau} G_k, \tag{5.2}$$

where μ_i^0 and τ_i^0 are the values of μ_i and τ_i in the case of absence of the applied fields and polarizability tensors κ_{ik} depend on the aggregate space configuration. The principal axes of these tensors are rigidly attached to the aggregate body. In this case the energy of the aggregate in the external field $U = -(\vec{\mu}\vec{H}) - (\vec{\tau}\vec{G})$ with the use of Eq.(5.2) can be written in the form

$$U = -(\vec{\mu}^0\vec{H}) - (\vec{\tau}^0\vec{G}) - \kappa_{ik}^m H_i H_k - \kappa_{ik}^{\tau} G_i G_k - \kappa_{ik} H_i G_k; \qquad \kappa_{ik} = \kappa_{ik}^{m\tau} + \kappa_{ki}^{\tau m}. \tag{5.3}$$

Note that the traces of tensors, which are in front of the combinations H_iH_k, G_iG_k and H_iG_k, can be omitted in this expression as they do not depend on the orientation angles of the aggregate.

In the case of low fields, the distribution function can be written in the form $W(\Omega) = C(1 - U/kT)$. Putting into this expression the energy from Eq.(5.3) and integrating over the orientation angles, one can find the mean values of magnetic and toroid moments of the suspension

$$\vec{M} = \frac{N}{3kT}\{[\mu_0^2 + \kappa_{ik}^m(\frac{4}{5}\kappa_{ik}^m H^2 + (\frac{3}{5}\kappa_{ik}^{m\tau} + \frac{1}{10}\kappa_{ik})(\vec{H}\vec{G})]\vec{H} +$$

$$+[(\vec{\mu}_0\vec{\tau}_0) + \frac{1}{10}\kappa_{ik}^m(\kappa_{ik} + 2\kappa_{ik}^{\tau m})H^2]\vec{G}\};$$

$$\vec{T} = \frac{N}{3kT}\{[(\vec{\mu}_0\vec{\tau}_0) + (\frac{4}{5}\kappa_{ik}^m\kappa_{ik}^{\tau m}H^2 + (\frac{1}{5}\kappa_{ik}^{\tau m}\kappa_{ik}^{m\tau} + \frac{6}{5}\kappa_{ik}^m\kappa_{ik}^\tau)(\vec{H}\vec{G})]\vec{H} +$$

$$+[\tau_0^2 + \frac{1}{10}\kappa_{ik}^m(3\kappa_{ik}^{\tau m}\kappa_{ik}^{m\tau} - 4\kappa_{ik}^\tau\kappa_{ik}^m)H^2]\vec{G}\}. \quad (5.4)$$

It was assumed in these calculations that the tensors $\kappa_{ik}^{m\tau}$ and $\kappa_{ik}^{\tau m}$ are symmetrical. Moreover, for the simplicity it was assumed that the vectors $\vec{H}$ and $\vec{G}$ are parallel to each other and we restrict ourselves only to the first oder of smallness with respect to the field $\vec{G}$.

The most important qualitative result which follows from these formulae is non-linear (quadratic) dependence of magnetization M on the magnetic field for the low fields (the initial susceptibility has linear dependence on the field when $\mu^0 = 0$). It is just the dependence which is observed experimentally for the aggregated suspensions [1-4]. Certainly, to answer the question which cause of this effect is the most important - the spread of particle sizes or the aggregate polarization considered here – the additional measurements of toroid susceptibility are needed. It is obvious that unaggregated particles, which are uniformly magnetized, do not contribute to this quantity.

When the applied fields are not low, the magnetic and toroid moments can be calculated with the help of the distribution function (5.1). But in this case the multidimentional integrals have to be calculated which produce considerable difficulties. Instead of that, the following appoximate method can be used. We suppose that the aggregate is at rest and the fields $\vec{H}$ and $\vec{G}$ rotate randomly over it. The values of the fields and the angles of their mutual orientation are the given quantities. In this case, the distribution function will depend on the Eulerian angles determining the orientation of the frame of reference connected with the vectors $\vec{H}$ and $\vec{G}$ relatively to the aggregate. The numerical procedure can be used to find the orientation of magnetic moments of the embryons for given field orientations. For any Ω one can calculate the values $U_m(\Omega, H, G)$, $\mu(\Omega, H, G)$ and $\tau(\Omega, H, G)$ This procedure is described in the sec. 3. After that, the averaging with respect to Ω can be performed with the help of a distribution function of the form

$$dW(\Omega) = C\ exp\{-U_m(\Omega, H, G)/kT\}d\Omega. \quad (5.5)$$

The numerical calculation of this kind was made for the aggregate which consists of four particles in a square shape. Figure 3 shows the average magnetic and toroid moments versus the fields ξ and ζ for different temperatures. The same figure shows the analogous curves for the rigid aggregate with frozen-in moments and superparamagnetic agrregate.

The tangent of the inclination angle of the curves on their initial interval is proportional to the initial susceptibilities χ_0^M and χ_0^T. The value χ_0^M is not dependent on the temperature (at the same time for the unaggregated suspension it was $\chi_0^M \sim 1/kT$) and toroid susceptibility χ_0^T is reciprocal to the temperature. A behaviour of that type follows from the "antiferromagnetic" structure of square aggregates, as it has been proposed in works [4-5]. We will consider this dependence elsewhere.

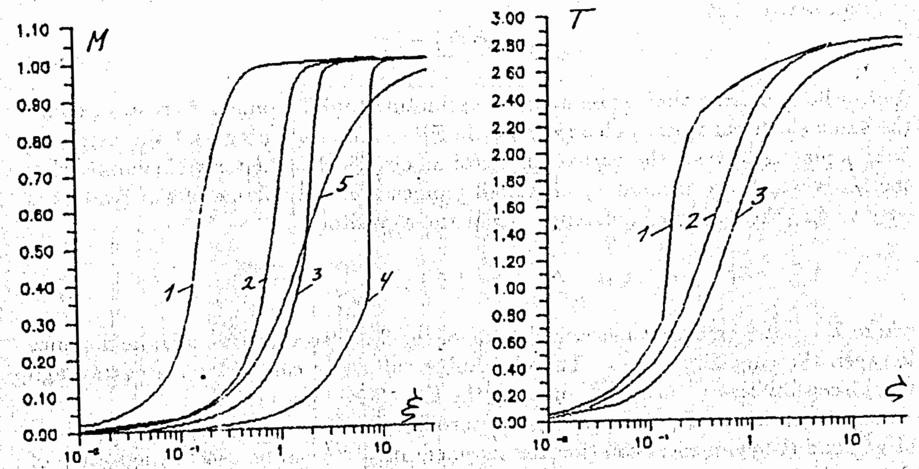

Fig. 3. *Magnetic $\vec{M}$ and toroidal $\vec{T}$ moments of the suspension of four-particles aggregates (square in form ones) (model of moving dipoles) against non-dimensional fields ξ and ζ for different values of undimensional temperature $\beta = V_0/kT$ (it is equal to 0.1, 0.5, 1 and 5 for the curves 1, 2, 3 and 4 on the fig.(a) and to 0.1; 4 for the curves 1, 2 on the fig.(b)). The Langevin function is also shown on the figures (the curves 5 (on the fig.a) and 3 (fig.b)) for comparison. This function describes the limit cases of super-paramagnetic aggregates (fig.a) and rigid aggregates (on the fig b).*

6. Measurement of toroid susceptibility of a suspension

In this part we discuss shortly the principle scheme of device for measurements of toroid susceptibility as the last one is rather new physical quantity. Note first, that for measuring of magnetic susceptibility the magnetization of a sample has to be varied in time (this variation can be produced, for example, by the additional "measuring" alternative magnetic field, rotation or vibration of the sample and so on). In this case the EMF is induced in the receiver coil.

The measurement of toroid susceptibility can be done by the similar way. The static toroid moment $\vec{\tau}$ does not induce around itself neither electrical, nor magnetic field but only the field of vector potential

$$\vec{A} = \frac{3\vec{r}(\vec{\tau}\vec{r}) - \vec{\tau}r^2}{r^5}. \qquad (6.1)$$

Let us suppose that moment $\vec{\tau}$ is varied in time ($i.e. \vec{\tau} = \vec{\tau}(t)$). Consequently, the alternative field of vector potential $\vec{A}(t)$ aroses around sample. This field, in its turn, leads to the appearance of electrical field $\vec{E} = -\dot{\vec{A}}/c$. Taking into account Eq. (6.1), one can derive that :

$$\vec{E} = -\frac{3\vec{r}(\dot{\vec{\tau}}\vec{r}) - \dot{\vec{\tau}}r^2}{cr^5}. \qquad (6.2)$$

As can be seen from this expression, the oscillating toroid moment $\vec{\tau}$ creates exactly the same electrical field as electrical dipole $\vec{p} = -\dot{\vec{\tau}}/c$. Assuming that the magnetic fluid is placed between the parallel plates of an electrical capacitor and summarizing the fields which are created by all toroid moments in the volume of the fluid, it is easy to find the potential difference $\Delta\varphi$ at the capacitor :

$$\Delta\varphi = 4\pi \mid \dot{\vec{T}} \mid d/c, \qquad (6.3)$$

where $\vec{T}$ is toroid moment per unit volume of the fluid (toroidness), d is the distance between the capacitor plates. The observable value $\Delta\varphi$ can be expressed through the susceptibilities χ^T and χ^{TM} in using the Eq. (2.9).

As shown in Fig 4.a and 4.b, the toroid induction coil (for the measurement of χ^T) and the cylindrical coil (for measurement of χ^{TM}) can be used for agitation of the oscillation of toroid polarization. Note that these devices are fully reversible, i.e. if alternating current is passed through the capacitor, than EMF will be induced in the coil (in this case the EMF will be proportional to χ^T in toroidal coil and EMF will be proportional to χ^{MT} in cylindrical one).

Toroid susceptibility of magnetic fluid may be also found from its contribution to the effective electrical permittivity of a suspension. Let us suppose that the alternating potential difference $\Delta\varphi \sim e^{-i\omega t}$ is applied to the capacitor plates (Fig. 4.c). In this case the displacement currents induce the vortex field on the sample. The value of the vorticity $\vec{G}$ is equal to $\vec{G} = rot\vec{H} = -i\omega\varepsilon_0\vec{E}_0/c$ (here $\vec{E}_0$ is an electrical field inside the capacitor when the sample is absent, ε_0 – is the electrical permittivity of the magnetic fluid, if the toroid polarization of the fluid is not taken into account). In accordance with the Eq.(2.9) the toroid polarization of a suspension $\vec{T} = \chi^T\vec{G} = -i\omega\varepsilon_0\chi^T\vec{E}_0/c$ aroses under the action of the vortex field. As it was shown above the value $-\dot{\vec{T}}/c$ is equivalent to the electrical polarization $\vec{P} = -\dot{\vec{T}}/c = \omega^2\varepsilon_0\chi^T\vec{E}_0/c^2$. Putting this expression into the formula $\vec{D} = \varepsilon_0\vec{E}_0 + 4\pi\vec{P}$ we can write the flux density in the form $\vec{D} = \varepsilon\vec{E}_0$, where the effective permittivity is introduced

$$\varepsilon = \varepsilon_0(1 + 4\pi\omega^2\chi^T/c^2). \qquad (6.4)$$

It follows from this expression that the effective permittivity ε depends on the frequency ω, i.e., the dispertion of the permittivity takes place. It has to be taken into

account that the value χ^T itself depends on the frequency. In the simplest approximation it may be proposed that it is equal to $\chi^T = \chi_0^T/(1 - i\omega\tau_p)$, where relaxation time τ_p is introduced.

In deriving Eq.(6.4) the phase difference between the current in the capacitor and the potential difference on its plates was not taken into account. Let us write the interaction energy of magnetic fluid with the vortex field in the form

$$U = -(\vec{T}\vec{G})V = -\chi^T\dot{E}^2V/c^2, \qquad (6.5)$$

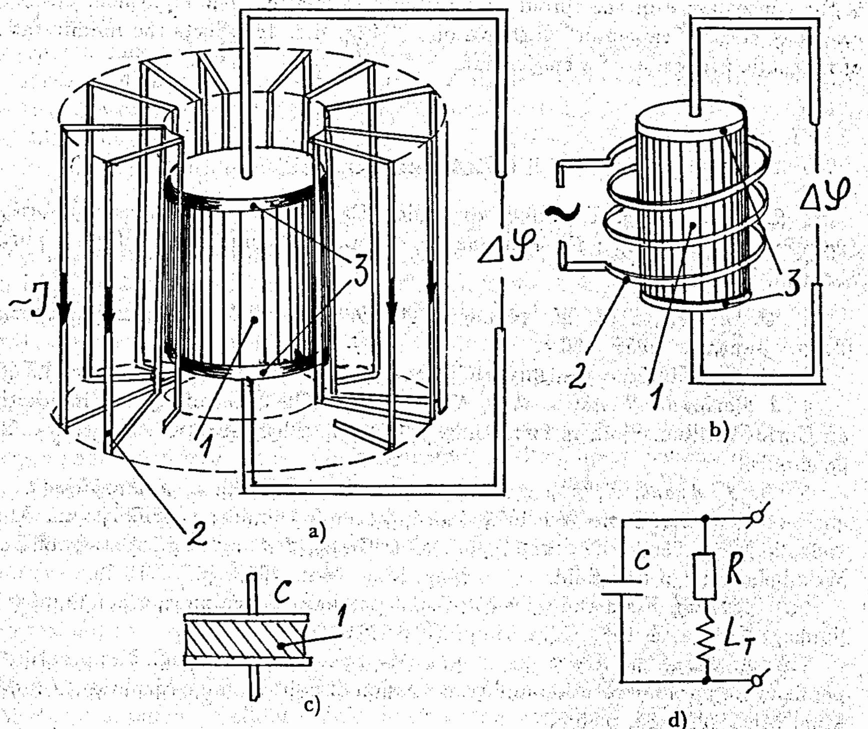

Fig. 4. *The cylinder-shaped sample with magnetic fluid 1 is inserted either into the toroidal induction coil (fig.a) or into cylindrical coil (fig.b) to take measurements of toroid susceptibilities χ^T and χ^{TM} respectively. When an alternating current is passed through the coil the magnetic field is produced on the sample (either the vortex one (fig.a) or uniform one (fig.b)). As a result the oscillation of toroid polarization takes place and the potential difference arises across the capacitor 3. Toroid contribution to this voltage can be determined from the Eq. (6.3). The capacitor filled by aggregated magnetic fluid and it's equivalent electrical circuit are shown on the fig. c and fig. d, respectively.*

where V is the volume of the fluid between the capacitor plates (Fig. 4.c). The electrical field E in the plane capacitor with the capacitance C is connected to the charge q on the capacitor plates by the equation $E = q/Cd$. As the current in the electrical circuit is equal to $J = \dot{q}$ and the capacitance is given by the expression $C = \varepsilon S/4\pi d$, Eq. (6.5) may be written in the form

$$U = -L_T J^2/2c^2; \qquad L_T = 8\pi\chi^T/\varepsilon C, \tag{6.6}$$

where the effective capacity inductance L_T is introduced. The origin of this quantity is the consequance of the toroid susceptibility existence. The equivalent electrical circuit of such a "capacitor" is shown on Fig. 4.c. It reflects the manifestation of magnetic properties of a suspension.

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