

Magnetic properties of dense ferrofluids: An influence of interparticle correlations

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A statistical model has been developed describing the magnetostatic properties of dense ferrocolloids and the dielectric properties of polar fluids. The model is based on the relation between the magnetization and the pair correlation function of a spatially homogeneous system of dipole particles. This approach allows us to calculate the ferrofluid magnetization (polarization density of polar fluid) in a form of expansion over both the particle concentration and the potential of the interparticle dipole-dipole interaction U_d . The obtained expressions for the ferrocolloid initial magnetic susceptibility, the dielectric constant of polar fluid and the ferrofluid magnetization with the accuracy $\sim U_d^2$ describe well the experimental data and the results of computer modeling. The model justifies the validity of the ‘‘modified mean-field approach,’’ and the effective field is calculated as a function of the Langevin magnetization.

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I. INTRODUCTION

Ferrofluids (ferrocolloids, magnetic fluids) are stable colloidal suspensions of the one-domain particles of ferromagnetic and ferrimagnetic materials in liquid carriers [1]. The small sizes of dispersed ferroparticles (diameter $d \sim 10$ nm) provide the particles with an inherent magnetic moment proportional to the volume of their magnetic grains. The stabilization of suspension is usually obtained by coating of magnetic grains with surfactant layers or by using of classical mechanism of double electric layer formation. As a result, the ferroparticles interact with each other through the spherically symmetric energy (steric repulsion, van der Waals attraction, electrostatic repulsion) and the noncentral dipole-dipole interaction of particle magnetic moments so that the ferrocolloid has much in common with a polar fluid. The high fluidity of ferrocolloids is combined with a perceptible ability to interact with an external magnetic field, which is the essence of their practical application.

An evaluation of magnetic characteristics of homogeneous ferrofluids comes up against the well-known problem of taking into account the interparticle dipole-dipole interaction. The latter is most conspicuous in concentrated systems and controls the correlations in mutual position of ferroparticles and in mutual orientation of their magnetic moments. In this sense, the problem is similar to calculation of dielectric properties of polar fluids. The literature on the last subject is quite extensive; considerable attention has been given by Debye [2], Onsager [3], Kirkwood [4], Wertheim [5]. Nonetheless, the problem of influence of interparticle correlations in dense polar fluids with intensive dipole-dipole interaction should not be considered as solved.

As far as the ferrofluids are concerned, the physical properties of dilute systems are well described in the framework of the one-particle model [6], which treats ferrocolloid as an ideal paramagnetic gas of particles, suspended in a liquid carrier. The equilibrium magnetization is written by applying the Langevin function, and the initial magnetic susceptibility χ_L is proportional to particle concentration n , mean squared particle magnetic moment $\langle m^2 \rangle$ and is inverse to temperature kT , that is, $\chi_L = n \langle m^2 \rangle / 3kT$. However, experiments with

concentrated ferrocolloids reveal an essential deviation from the Langevin formulas [7]. The initial susceptibility increases faster than that according to linear dependence $\chi_L \sim n$. The same behavior is also typical for the polar fluids [8].

It is clear that this deviation is primarily due to the interparticle interactions. A number of theoretical models allow the evaluation of the magnetic properties taking into account the dipole-dipole interactions, these are different variants of the mean-field model [2,3,9,10], the mean-spherical model [5,11,12], and the thermodynamic perturbation model [13,14]. In the framework of the most popular mean-field model by Weiss [2,9] the dipole-dipole interactions are assumed to be equivalent to some increase in the intensity of an external magnetic field, with the amount of its contribution being proportional to magnetization M of the ferrocolloid. The effective field acting on a single-domain particle is expressed as $H_e = H + \kappa M$. The mean-field constant is generally assumed to be equal to the Lorentz value $\kappa = 4\pi/3$. In this case H_e coincides with a field intensity in the spherical cavity formed by a particle in a liquid, provided that the cavity itself exerts no effect on the state of the neighboring particles. Thus, this model yields the Curie-Weiss law for the initial susceptibility $\chi = \chi_L / (1 - \kappa \chi_L)$. The Weiss model predicts a magnetic phase transition into a magneto-ordered liquid state; at the transition point the initial susceptibility becomes infinite, that is, $\chi \rightarrow \infty$ when $\chi_L \rightarrow 3/4\pi$. But a paramagnetic to ferromagnetic second order phase transition is never observed in fluidlike magnetic systems. That is why the Weiss mean-field theory appears to be questionable while applying to magnetic fluids (or polar fluids).

The mean-field Onsager model [3] is based on the assumption that the cavity formed by a particle in a ferrofluid influences the orientation of the magnetic moments of the neighboring particles. The initial susceptibility remains finite for any finite temperature and concentration, but the experimental and computer studies have shown that the Onsager model highly underestimates the values of the initial susceptibility of concentrated ferrocolloids (as well as the dielectric constant of polar fluids) [7,13,15,16].

Attempts to use the mean-spherical model [11,12] and the

thermodynamic perturbation method [13,14] proved far more successful. These models are appropriate to describe well experimental data on magnetostatic properties of real magnetic fluids. Obviously, these models have the coincident fields of adequacy and are valid for ferrocolloids with low or moderate concentrations of magnetic phase $\sim 10\text{--}12\%$ under the presence of an arbitrarily valued uniform magnetic field.

The most precise description of the magnetization curves of moderately concentrated ferrofluids is given by the so-called ‘‘modified mean-field model’’ [10]. This approach is based on the assumption that the effective field acting on a ferroparticle is proportional to the Langevin magnetization M_L , that is, $H_e = H + (4\pi/3)M_L$. The resulting expressions for the initial susceptibility $\chi = \chi_L(1 + 4\pi\chi_L/3)$ and for the magnetization in saturation conditions are coincident with the predictions of the thermodynamic perturbation model [13,14]. But the modified mean-field model gives the more accurate description of the magnetization curves in the arbitrary external field strengths.

All the last-mentioned models are valid in the case when the intensity of interparticle dipole-dipole interaction does not exceed by the order of value of the thermal energy kT . It means that the dipole-dipole interaction parameter $\gamma = m^2/d^3kT$, having a meaning of the interaction energy of the two contacting particles related to the thermal energy, has the order of unity or less, that is, $\gamma \lesssim 1$. For dense ferrofluids with a magnetic phase concentration over $15\text{--}18\%$ or ferrofluids, consisting of large particles, this is insufficient. The temperature dependencies of the initial susceptibility of these systems demonstrate the large deviations [7,17] between the theoretical predictions and the experimental data. At low temperatures the models [10,11,13] underestimate the values of initial susceptibility by $15\text{--}20\%$. It is clear that this deviation is due to the fact that the dipole-dipole interactions are most conspicuous in concentrated magnetic fluids.

Besides the mentioned, other methods are recruited to evaluate the dielectric constant of polar fluids. For example, the hypernetted chain approximation [18] leads to the highly overestimated values in comparison with the results of computer modelling [8,19,20]. The likewise overestimation of the dielectric constant is given by the recently developed algebraic perturbation model [15]. In the region of moderate values of dielectric constant $\epsilon \sim 30$, the computer results are well described by the perturbation model developed in Ref. [21]. However, the theories mentioned are valid only for weak external fields and do not consider the dependence of polarization density in an arbitrarily valued electric field.

This leads to the conclusion that the role of dipole-dipole interaction in dense dipolar fluidlike systems is not studied theoretically well. This problem seems to be of principal nature and to be of specific interest for many fields of applied science.

In the present paper we focus our attention on a new approach connecting the macroscopic ferrofluid magnetization with the pair correlation function of ferroparticle system (Sec. II). Applying to dense ferrocolloids we have calculated the pair correlation function with the help of the first order

perturbation method over the intensity of dipole-dipole interaction under the presence of a uniform external magnetic field (Sec. III). We have obtained the exact expression for the initial susceptibility on the basis of the second order over such perturbation. We have shown the statistical way leading to the Weiss mean-field model. The results of the model (Secs. II and III) are tested on the polar fluids in Sec. IV. We have calculated the dielectric constant both for the dipolar hard-sphere fluid and for the Stockmayer fluid. Our results describe well the data of computer modeling and substantiate that the dielectric constant of dense polar fluids is influenced not only by the dipole-dipole interaction but the central interparticle energy as well. In Sec. V we study the initial susceptibility of dense magnetic fluids. The analysis shows that the magnetic properties of ferrocolloids are weakly dependent on the method of stabilization of suspension. For the first time we have obtained a precise description of the temperature dependence of initial susceptibility at low temperatures ($4\pi\chi \sim 60\text{--}80$). Attempts to use the second order perturbation model for magnetization curves allows us to justify the modified mean-field model and to suggest the statistical method of determination of the effective field (Sec. VI). We have proposed a simple expression for magnetization in a form of modified mean-field theory that describes very accurately the total magnetization curves of ferrofluids with the maximum allowable concentration of a magnetic phase $\sim 18\%$.

II. FERROFLUID MAGNETIZATION AND PAIR INTERPARTICLE CORRELATIONS

Presenting a general method, let us consider first a monodisperse liquid system of N identical spherical particles (diameter d) containing the constant magnetic moment m (dipole moment). The particles are suspended in a neutral liquid carrier of the volume V . Each particle i is characterized by a radius-vector $\mathbf{r}_i(r_i, \theta_i, \varphi_i)$ and by a vector $\mathbf{\Omega}_i(\omega_i, \zeta_i)$, describing the orientation of its magnetic moment $\mathbf{m}_i = m\mathbf{\Omega}_i$. Now it is necessary to discuss the shape of the volume with a ferrofluid. It is well known [22] that under the presence of a magnetic field the thermodynamic properties of magnetic media are dependent on their shapes due to the demagnetization effects. Since we are going to study the magnetic properties of ferrofluids as a function of an external field, we choose the shape of a container with ferrofluid such that the influence of demagnetization field can be neglected. Thus, we consider the volume of the system in a shape of infinitely elongated ellipsoid of revolution (the ratio of the minor to major ellipsoid semiaxis should tend to zero) stretched along an external uniform magnetic field \mathbf{H} . It is important to stress that using the infinitely elongated ellipsoidal shape is of advantage because this is just the case when demagnetization factors are of no consequence and do not need to be accounted for (the external magnetic field coincides exactly with the internal one). For more general shapes of the container, the demagnetization factor of the system needs to be taken into account.

The Hamiltonian \hat{H} contains the following terms: the spherical part of interparticle interaction $U_s(ij)$ (hard sphere

interaction, van der Waals forces, electrostatic repulsion); the dipole-dipole interaction $U_d(ij)$ of the particle magnetic moments; and the interaction of magnetic moments with an external field $U_m(i)$

$$\hat{H} = \hat{H}_d + \hat{H}_s + \hat{H}_m, \quad \hat{H}_s = \sum_{i < j = 1}^N U_s(ij), \quad (1)$$

$$\hat{H}_d = \sum_{i < j = 1}^N U_d(ij),$$

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

$$\hat{H}_m = \sum_{i=1}^N U_m(i) = -mH \sum_{i=1}^N \cos \omega_i, \quad \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j.$$

The partition function \tilde{Q} may be written in the form

$$\tilde{Q} = (\sinh \alpha / \alpha)^N Q, \quad Q = \prod_{i=1}^N \hat{R}_i \prod_{i=1}^N \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d), \quad (2)$$

$$\hat{R}_i f(\mathbf{r}_i) = \frac{1}{V} \int f(\mathbf{r}_i) d\mathbf{r}_i,$$

$$\hat{\Omega}_i f(\boldsymbol{\Omega}_i) = \frac{\alpha}{\sinh \alpha} \int f(\boldsymbol{\Omega}_i) \exp(\alpha \cos \omega_i) d\boldsymbol{\Omega}_i,$$

$$\alpha = mH/kT, \quad \beta = 1/kT,$$

$$d\boldsymbol{\Omega}_i = (4\pi)^{-1} \sin \omega_i d\omega_i d\zeta_i,$$

$$d\mathbf{r}_i = r_i^2 dr_i \sin \theta_i d\theta_i d\varphi_i,$$

where the action of the operators \hat{R}_i and $\hat{\Omega}_i$ corresponds with the averaging over all positions of the i th particle in the volume V and over all orientations of the i th magnetic moment. In the integrals we use the following Cartesian (x, y, z) coordinate system: the coordinate origin is placed at the center of the ferrofluid volume; z axis is parallel to the major axis of the ellipsoid, that is, $\mathbf{H} \parallel Oz$; the angles ζ_i, φ_i are the polar angles in the plane $(x, y) \perp Oz$; the angles ω_i, θ_i are the angles between the vectors $\boldsymbol{\Omega}_i, \mathbf{r}_i$ and the direction of an external field (Oz axis).

Introducing the magnetization M by the definition

$$M = - \frac{1}{V} \frac{\partial}{\partial H} (-kT \ln \tilde{Q}), \quad (3)$$

we get the following expression (see Appendix A), connecting the magnetization with the one-particle distribution function $g_1(\mathbf{r}_i, \boldsymbol{\Omega}_i)$:

$$M(H) = nm \frac{1}{2} \int_0^\pi \cos \omega_1 g_1(\omega_1) \sin \omega_1 d\omega_1, \quad (4)$$

$$n = N/V, \quad \int g_1(\omega_1) d\boldsymbol{\Omega}_1 = 1.$$

This function represents actually a probability for a single particle to be placed at a point \mathbf{r}_i and to be oriented in a direction $\boldsymbol{\Omega}_i$. It is well known that for a homogeneous liquid state the equality $g_1(\mathbf{r}_i, \boldsymbol{\Omega}_i) \equiv 1$ holds true [23] in the case of the absence of an external field. Otherwise, this probability depends only on the angle ω_i between the external field direction and the orientation of the magnetic moment of a single particle, that is, $g_1(\mathbf{r}_i, \boldsymbol{\Omega}_i) \equiv g_1(\omega_i)$. For example, for an ideal paramagnetic gas [$U_s(ij) = U_d(ij) \approx 0$] from the definition of $g_1(\mathbf{r}_i, \boldsymbol{\Omega}_i)$ (Appendix A) one can easily get the well-known Langevin magnetization

$$g_1(\omega_1) = (\alpha / \sinh \alpha) \exp(\alpha \cos \omega_1), \quad (5)$$

$$M(H) = M_L(H) = nmL(\alpha), \quad L(\alpha) = \coth \alpha - 1/\alpha.$$

For the interacting particle system the expression (4) is not used practically. This is caused by the fact that there are no methods for determining one-particle distribution function in dense liquids. The main idea of our approach is that such a method may be formulated for a ferrofluid (polar fluid) placed in an external field. The method is based on the Bogolyubov-Born-Green-Kirkwood-Ivon (BBGKI) formalism [23] using the angle dependence of the function $g_1(\omega_1)$. Differentiating this function with respect to ω_1 we come to the equation, connecting the one-particle distribution function with the pair correlation function $g_2(\mathbf{r}_i, \mathbf{r}_j, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j) = g_2(ij)$ (see Appendix B):

$$\frac{dg_1(\omega_1)}{d\omega_1} = -\alpha \sin \omega_1 g_1(\omega_1) - \frac{n}{kT} \int d\boldsymbol{\Omega}_2 \int d\mathbf{r}_2 \frac{dU_d(12)}{d\omega_1} g_2(12). \quad (6)$$

The pair correlation function $g_2(\mathbf{r}_1, \mathbf{r}_2, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2)$ represents actually the mutual probability for two particles (1 and 2) to be placed at the points \mathbf{r}_1 and \mathbf{r}_2 and to be oriented along the directions $\boldsymbol{\Omega}_1$ and $\boldsymbol{\Omega}_2$. This probability is influenced both by the pair interparticle interaction $U_s(12) + U_d(12)$ and by the interactions $U_m(1)$ and $U_m(2)$ of the magnetic moments with an external field. It is convenient to introduce this function in a form (Appendix B)

$$g_2(12) = (\alpha / \sinh \alpha)^2 \exp[\alpha(\cos \omega_1 + \cos \omega_2)] \tilde{g}_2(12), \quad (7)$$

separating out the ideal paramagnetic terms [see expression (5)]. The function $\tilde{g}_2(12)$ describes all the multiparticle correlations in the mutual two-particle probability.

The analytical solution of Eq. (6) with respect to normalization condition (4) gives

$$g_1(\omega_1) = \frac{\alpha}{\sinh \alpha} \exp(\alpha \cos \omega_1) \left[1 + (1 - \hat{\Omega}_1) \frac{n}{kT} \right. \\ \left. \times \int d(\cos \omega_1) \hat{\Omega}_2 \int d\mathbf{r}_{12} \frac{dU_d(12)}{\sin \omega_1 d\omega_1} \tilde{g}_2(12) \right], \quad (8)$$

$$M(H) = M_L(\alpha) + \frac{n^2 m}{kT} \hat{\Omega}_1 \hat{\Omega}_2 [\cos \omega_1 - L(\alpha)] \\ \times \int d(\cos \omega_1) \int d\mathbf{r}_{12} \frac{dU_d(12)}{\sin \omega_1 d\omega_1} \tilde{g}_2(12). \quad (9)$$

Here we use the fact that the spatial two-particle probability depends only on the mutual interparticle distance \mathbf{r}_{ij} , that is, $\tilde{g}_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{\Omega}_1, \mathbf{\Omega}_2) = \tilde{g}_2(\mathbf{r}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$. The integration $d(\cos \omega_1)$ means the indefinite integral with respect to $\cos \omega_1$, arising from the solution of equation (6). The expression (9) is exact and includes all the corrections to the Langevin magnetization influenced by a multiparticle correlation. Besides that, the expression (9) is of principal nature. On its basis the cluster expansion methods may be developed to determine the ferrofluid magnetization (polar fluid polarization) in the arbitrary values of an external field. An important feature of the method is that the right-hand parts of expressions (8) and (9) contain the first orders of particle concentration n and dipole-dipole interaction potential U_d . Thus, the determination of the pair correlation function $\tilde{g}_2(12)$ up to the order of $\sim n^k, U_d^k$ gives the magnetization in terms of the order $\sim n^{k+1}, U_d^{k+1}$.

To demonstrate this advantage let us consider the expansion of $\tilde{g}_2(12)$ with zero-order accuracy over the dipole-dipole potential (zero-order perturbation). In this case we assume that all interparticle correlations are controlled by the spherical part of the interparticle interaction energy $U_s(ij)$, that is, $\tilde{g}_2(ij) = g_s(ij)$. Here $g_s(ij)$ stands for the pair distribution function of the reference system [system of particles, interacting through the central interparticle energy $U_s(ij)$ only]. Substituting the function $g_s(12) \equiv g_s(|\mathbf{r}_1 - \mathbf{r}_2|)$ in expressions (8) and (9) we come up against the problem of averaging of the first order of dipole-dipole interaction U_d over all the positions of particles 1 and 2. It was shown in Refs. [13,22] that the result of this integration depends on the shape of the system (but does not depend on the volume and on the type of the central interparticle interaction). For the case of infinitely elongated ellipsoidal container with the neglecting influence of demagnetization effects we get

$$g_1(\omega_1) = \frac{\alpha}{\sinh \alpha} \exp(\alpha \cos \omega_1) \left\{ 1 + \frac{4\pi}{3} \frac{nm^2}{kT} L(\alpha) \right. \\ \left. \times [\cos \omega_1 - L(\alpha)] \right\}, \quad (10)$$

$$M(H) = M_L(H) \left[1 + \frac{4\pi}{3} \frac{dM_L(H)}{dH} \right],$$

$$\chi = \chi_L \left(1 + \frac{4\pi}{3} \chi_L \right), \quad \chi_L = nm^2/3kT,$$

where the initial magnetic susceptibility χ is presented in quadratic parabola behavior over the Langevin susceptibility χ_L . This result coincides with the prediction of the first order perturbation theory [13] and is independent on the spherical part on interparticle energy U_s . It should be noted that the comparison of the one-particle correlation function in forms (5) and (10) shows that the consideration of the magnetic interaction U_d on the basis of the first order perturbation theory results in the more pronounced orientation of ferrofluid particles along an external field direction.

III. SECOND ORDER PERTURBATION MODEL

The results (10) of the first order perturbation model describe well the magnetic properties of the moderately concentrated ferrofluids (magnetic phase concentration $\sim 10 - 12\%$) [7,13] as well as the high-temperature dielectric properties of polar fluids [16]. For the dense ferrofluids at low temperatures (intensive dipole-dipole interaction) it is insufficient. The experimental studies [7,17] of temperature dependences of the initial susceptibility of highly concentrated magnetic fluids (magnetic phase concentration $\sim 18\%$) have demonstrated the disagreement between the theoretical predictions and the experimental data.

The determination of the pair correlation function $\tilde{g}_2(12)$ in terms of higher orders of perturbation method comes up with the following problem: the cluster expansion results for the pair distribution function [23] become invalid under the presence of an external field. This problem manifests itself in multiparticle correlations and is caused by the change of the topological properties of the corresponding graphs. These graphs must consider not only the various combinations of the orders of dipole-dipole interaction, but the interaction of the graph tops (particle magnetic moments) with an external field as well. As a result, the topological structure of the cluster expansion varies drastically.

Let us consider all the corrections of the first order of $U_d(ij)$ in pair correlation function,

$$\tilde{g}_2(12) = [1 - \beta U_d(12)] g_s(12) + \Delta \tilde{g}_2(12), \quad (11)$$

$$\Delta \tilde{g}_2(12) = \exp[-\beta U_s(12)] n \left\{ \int d\mathbf{r}_3 \hat{\Omega}_3 [-\beta U_d(13) \right. \\ \left. - \beta U_d(23)] \exp[-\beta U_s(13) - \beta U_s(23)] \right. \\ \left. - 2 \int d\mathbf{r}_{34} \hat{\Omega}_3 \hat{\Omega}_4 [-\beta U_d(34)] \right. \\ \left. \times \exp[-\beta U_s(34)] \right\}.$$

The correction term $\Delta \tilde{g}_2(12)$ coincides with the classical result [23] only in the absence of an external field ($\alpha=0$). In this case the last term on the right-hand side of expression for $\Delta \tilde{g}_2(12)$ compensates in part the first term. This compen-

sation leads to the dependence of pair correlation function on the Mayer functions $f_d(ij) = \exp[-\beta U_d(ij)] - 1$ in the total graph expansion. Under the presence of an external field such compensation does not take place. Naturally, we would calculate the function $\Delta \tilde{g}_2(12)$ for the system of dipolar hard spheres, that is, $U_s(ij) = U_{HS}(ij)$,

$$\Delta \tilde{g}_2(12) = n \exp[-\beta U_{HS}(12)](I_1 + I_2 - 2I_3), \quad (12)$$

$$I_j = \int d\mathbf{r}_3 \hat{\Omega}_3 [-\beta U_d(j3)] \exp[-\beta U_{HS}(13) - \beta U_{HS}(23)], \quad j=1,2,$$

$$I_3 = \int d\mathbf{r}_{34} \hat{\Omega}_3 \hat{\Omega}_4 [-\beta U_d(34)] \exp[-\beta U_{HS}(34)].$$

The last one I_3 is the simplest:

$$\begin{aligned} I_3 &= \frac{1}{kT} \int d\mathbf{r}_{34} \hat{\Omega}_3 \hat{\Omega}_4 \left[3 \frac{(\mathbf{m}_3 \mathbf{r}_{34})(\mathbf{m}_4 \mathbf{r}_{34})}{r_{34}^5} - \frac{(\mathbf{m}_3 \mathbf{m}_4)}{r_{34}^3} \right] \\ &\quad \times \exp[-\beta U_{HS}(34)] \\ &= \frac{m^2}{kT} L(\alpha)^2 \int d\mathbf{r}_{34} \frac{3(\hat{r}_{34} \hat{z})^2 - 1}{r_{34}^3} \\ &\quad \times \exp[-\beta U_{HS}(34)]. \end{aligned} \quad (13)$$

Here \hat{r}_{34} and \hat{z} are the unit vectors ($\mathbf{r}_{34} = r_{34} \hat{r}_{34}, \hat{z} \parallel \mathbf{H}$) and we use $\hat{\Omega}_i \mathbf{m}_i = m \hat{z} L(\alpha)$.

While calculating the integral over $d\mathbf{r}_{34}$ we must take into account the infinitely elongated ellipsoidal shape of the container [14],

$$\int d\mathbf{r}_{34} \frac{3(\hat{r}_{34} \hat{z})^2 - 1}{r_{34}^3} \exp[-\beta U_{HS}(34)] = \frac{4}{3} \pi. \quad (14)$$

As a result, the last term in expression for the function $\Delta \tilde{g}_2(12)$ has the order of $\sim L(\alpha)^2$,

$$I_3 = \frac{4\pi m^2}{3 kT} L(\alpha)^2. \quad (15)$$

The terms I_1 and I_2 have the same structure. It is convenient to introduce it in the following form:

$$I_1 = J_{EV}(1) + J_{MF}(1), \quad (16)$$

$$\begin{aligned} J_{EV}(1) &= \int d\mathbf{r}_3 \hat{\Omega}_3 [-\beta U_d(13)] \exp[-\beta U_{HS}(13)] \\ &\quad \times \{\exp[-\beta U_{HS}(23)] - 1\}, \end{aligned}$$

$$J_{MF}(1) = \int d\mathbf{r}_{13} \hat{\Omega}_3 [-\beta U_d(13)] \exp[-\beta U_{HS}(13)].$$

The term J_{MF} corresponds to the averaging over positions and orientations of the third particle inside the first one, but

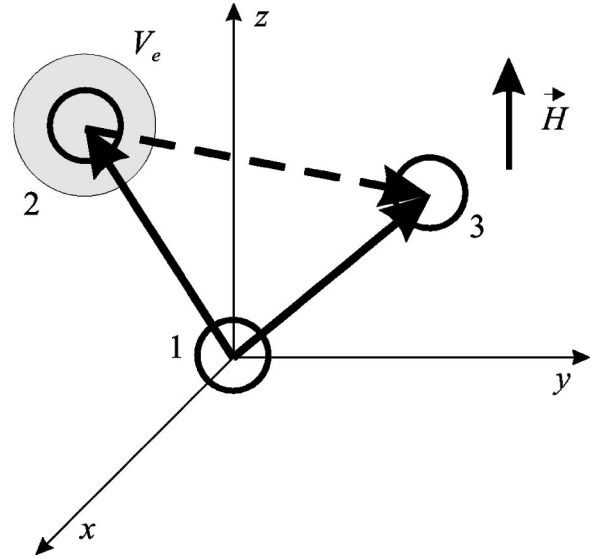


FIG. 1. Geometry of particle positions under the calculation of the pair correlation function. V_e is the excluded volume for the third particle.

in the total volume V . It is equivalent to the assumption of the mean-field model, when the position and orientation of the third particle are not influenced by the presence of the second one,

$$J_{MF}(j) = \frac{4\pi m^2}{3 kT} L(\alpha) \cos \omega_j, \quad j=1,2. \quad (17)$$

The term $J_{EV}(1)$ gives the corrections to $J_{MF}(1)$ resulting from the nonpenetrating conditions between the particles 2 and 3. The integration over $d\mathbf{r}_3$ in $J_{EV}(1)$ has to be made over the excluded volume V_e (Fig. 1),

$$J_{EV}(j) = -\frac{4\pi m^2}{3 kT} [3(\hat{r}_{12} \hat{m}_j)(\hat{r}_{12} \hat{z}) - (\hat{m}_j \hat{z})] L(\alpha) G(r_{12}), \quad (18)$$

$$j=1,2, \quad \mathbf{m}_j = \hat{m}_j m,$$

$$G(r_{12}) = \begin{cases} 0, & r_{12} < d \\ 3r_{12}/16d - r_{12}^3/32d^3, & d < r_{12} < 2d \\ d^3/r_{12}^3, & 2d < r_{12}. \end{cases}$$

The function $G(r_{12})$ is obtained with respect to the second virial term in the hard-sphere distribution function [23]. One can see that the terms I_1 and I_2 have the order $\sim L(\alpha)$ that differs from I_3 .

With the help of the results of this section it is easy to obtain the expression for the initial magnetic susceptibility. The consideration of the first term in Eq. (11) and J_{MF} parts only in $\Delta \tilde{g}_2(12)$ gives the following expression:

$$\chi = \chi_L [1 + 4\pi \chi_L / 3 + (4\pi)^2 \chi_L^2 / 9] \approx \chi_L / (1 - 4\pi \chi_L / 3), \quad (19)$$

which is not influenced by the first order of U_d and by the explicit form of the function g_s in the first term of the right-hand part of expression (11). Their contributions vanish in the limit $H \rightarrow 0$. The expression (19) represents the expansion of the mean-field model result with the cubic accuracy in χ_L . The divergence $\chi \rightarrow \infty, 4\pi\chi_L/3 \rightarrow 1$ (that is, the second order magnetic phase transition) is a result of neglect of interparticle correlations (excluded volume in Fig. 1). Taking into account J_{EV} terms we find the exact expression for χ with the cubic accuracy in χ_L ,

$$\chi = \chi_L [1 + 4\pi\chi_L/3 + (4\pi)^2\chi_L^2/144 + O(\chi_L^3)]. \quad (20)$$

We should note that the expressions (11)–(18) determine the pair correlation function of the dipolar hard-sphere fluid influenced by the pair and three-particle correlations with the accuracy $\sim U_d$. As it was mentioned earlier, this accuracy results in quadratic dependence of the magnetic characteristics on U_d . The three-particle terms (Fig. 1) take into account the dipole-dipole correlations in pairs of particles 1-2 and 1-3. But the particles 2 and 3 interact with each other only through the spherical energy U_s . In this case the addition to expression (10) term $(4\pi)^2\chi_L^3/144$ is positive. It means that the consideration of linear pair correlation function in U_d leads to much more pronounced orientation of ferroparticles along an external field direction than is predicted by the first order perturbation model. It is not a surprise, because only the circlelike graphs may lead to the opposite effects. But these graphs will appear only in the next, second order expansion of $\tilde{g}_2(ij)$ over U_d .

It is worth noting that the initial susceptibility (20) does not depend explicitly on the ferroparticle concentration n and on the magnetodipole interaction parameter γ , but depends only on the combination $\chi_L = nm^2/3kT$. In this way, the Langevin susceptibility χ_L represents the universal parameter, which determines the magnetic properties of ferrofluids in weak magnetic fields. This peculiarity is studied in detail in Sec. V.

IV. STATIC DIELECTRIC PROPERTIES OF POLAR FLUIDS

Since the expression (20) stands for one of the most important results of the present model, it should be tested on the experimental and numerical data. Unfortunately, we do not have the experimental data on the concentration dependence of the initial magnetic susceptibility for dense ferrofluids. That is why we refer to the polar fluids, the dielectric properties of which are well studied with the help of computer modeling methods.

Two main systems are traditionally used as the models of polar fluids, they are: the dipolar hard-sphere fluid and the Stockmayer fluid. For the first one, the central interaction $U_s(ij)$ is assumed to be the hard sphere potential $U_{HS}(ij)$. The Stockmayer fluid is comprised of particles with permanent dipole moments \mathbf{p} interacting with the Lennard-Jones potential,

$$U_s(ij) \rightarrow U_{LJ}(ij) = 4\epsilon_{LJ} [(d/r_{ij})^{12} - (d/r_{ij})^6], \quad (21)$$

as well as the dipole-dipole interaction (1).

The main result of a large number of theoretical models of dielectric properties of polar fluids is a presentation of the dielectric constant ϵ in a form of expansion over the parameter $y = 4\pi\chi_L/3 = (4\pi/9)(np^2/kT)$,

$$\epsilon - 1 = 3y(1 + y + Ay^2 + \dots). \quad (22)$$

All the theories give the coincident coefficients in the first and second terms of expansion (22). But the predictions of the third coefficient A are different. For example, the mean-field model by Debye [2], $A = 1$; the Onsager model [3], $A = -6$; the mean-spherical model by Wertheim [5], $A = 1/16$; the perturbation theory [21], $A = 1/16$; and the recently developed algebraic perturbation model [15], $A = 15/16$. The exact value of A follows from the second order perturbation theory (20): $A = 1/16 + O(n)$. Besides that, some models (see, for example, [15,21]) consider the corrections of the higher orders over concentration to the value of coefficient A , resulting from the account of multiparticle correlations. These additional terms depend on the concentration n , the dipole-dipole interaction parameter γ , and the Lennard-Jones energy ϵ_{LJ} . Thus, the universal expansion of dielectric constant ϵ over the susceptibility of ideal polar gas (22) holds true only for the sufficiently small values of y . The large number of computer simulations for dense polar fluids demonstrate the independent influence of parameters y, γ, ϵ_{LJ} on the dielectric constant. To study such an influence we have to take into account the second order terms over U_d in the pair correlation function (11). The point is that we have to consider first the pair dipole-dipole interactions, that is,

$$\begin{aligned} \tilde{g}_2(12) = & \{1 - \beta U_d(12) + [-\beta U_d(12)]^2/2\} g_s(12) \\ & + \Delta \tilde{g}_2(12). \end{aligned} \quad (23)$$

The additional term $\sim U_d^2$ to expression (11) is of the zero order over concentration n , while the corresponding terms in $\Delta \tilde{g}_2(12)$ are of the higher orders over n . Hence, the main term is the additional term (23), but never theoretical models have taken it into account. The dielectric constant may be easily calculated, assuming the simplest determination of the pair distribution function $g_s(12)$ of the reference model in zero order over concentration: $g_s(12) = \exp[-\beta U_s(12)]$. We get for the dipolar hard sphere fluid,

$$\epsilon - 1 = 3y[1 + y(1 + \gamma^2/25) + y^2/16], \quad (24)$$

and for the Stockmayer fluid,

$$\begin{aligned} \epsilon - 1 = & 3y \left\{ 1 + y \left[1 + \frac{\gamma^2}{25} \sqrt{\frac{\pi kT}{2\epsilon_{LJ}}} \exp\left(\frac{\epsilon_{LJ}}{kT}\right) \right. \right. \\ & \left. \left. \times \operatorname{erfc}\left(-\sqrt{\frac{\epsilon_{LJ}}{kT}}\right) + \frac{y^2}{16} \right] \right\}. \end{aligned} \quad (25)$$

Figures 2–4 show our results in comparison with the computer simulations. Figure 2 demonstrates the predictions of various theoretical models for the dipolar hard-sphere

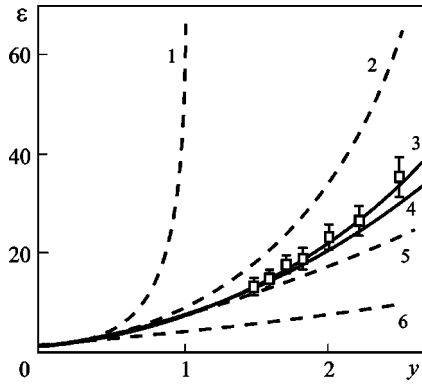


FIG. 2. Dielectric constant of the dipolar hard-sphere fluid. Points represent the computer calculations [20]; curves: 1, the mean-field model by Debye [2]; 2, the hypernetted chain approximation [18]; 3, the expression (24); 4, the expression (22) with $A = 1/16$; 5, the mean-spherical approximation [5]; 6, the mean-field model by Onsager [3].

fluid of density $\rho = nd^3 = 0.8$ [20]. The universal expansion (22) describes well the numerical results in the region $y < 2$. But for higher values $y \sim 3$ the discrepancy amounts up to 10–15%. The corrected expression (24) is the best due to the explicit dependence on the dipole-dipole interaction parameter $\gamma \sim 2$ [20].

The comparison of expressions (22), (24), and (25) with the computer simulations [8] on the Stockmayer fluid ($\rho = 0.8, \epsilon_{LJ} = kT/1.35$) is presented in Fig. 3. It follows that the Stockmayer fluid is characterized by the larger values of dielectric constant as compared with the dipolar hard spheres of the same concentration and dipole moments. The fact is that the Stockmayer particles are more pair correlated due to the influence of the attractive part of Lennard-Jones potential.

The explicit dependence of dielectric constant of polar fluid on the dipole-dipole interaction parameter γ is shown in Fig. 4. Both the numerical results [19] ($\epsilon_{LJ} = kT/1.15$) and the expression (25) predict the faster increase of ϵ than it follows from the universal expansion (22). So, we come to the conclusion that the static dielectric properties of dense polar fluids are greatly dependent on the form and intensity

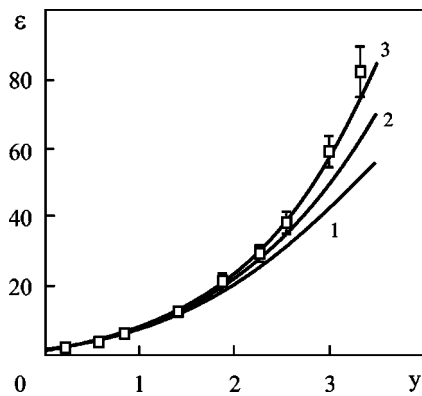


FIG. 3. Dielectric constant of the Stockmayer fluid. Points represent the computer calculations [8]; curves: 1, the expression (22) with $A = 1/16$; 2, the expression (24); 3, the expression (25).

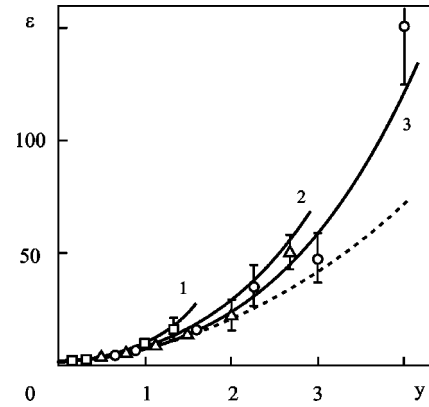


FIG. 4. Dielectric constant of the Stockmayer fluid. Solid curves 1–3 represent the expression (25); dashed curve represents the universal expansion (22) with $A = 1/16$; points represent the computer calculations [19] at $\rho = 0.274$ (\diamond and 1), 0.548 (\triangle and 2) and 0.822 (\circ and 3).

of the spherical part of interparticle interaction energy. This is caused by the fact that the central interaction $U_s(ij)$ results in the spatial correlations between particles and implicitly influences the orientational correlations between the particle dipole moments.

Figure 5 shows the influence of the dipole-dipole interaction on the polarization density P of polar fluid in the arbitrary values of a uniform electric field E . Points correspond to the computer simulations [8] for Stockmayer fluid ($\rho = 0.8, \epsilon_{LJ} = kT/1.35, \gamma = 0.74, \epsilon = 5.4$). The polarization density of an ideal polar gas (curve 1) greatly underestimates the results of numerical modeling. Otherwise, the first order perturbation model (10) overestimates (curve 2) the polarization density for the moderate external field strengths ($Ep/kT \sim 1$). The very accurate description is given by the modified mean field model (dashed curve), developed in Sec. VI.

V. INITIAL SUSCEPTIBILITY OF DENSE MAGNETIC FLUIDS

Formally, the conclusion of the previous section about the influence of central interparticle correlations should be also fulfilled for ferrofluids. Nonetheless, the experimental studies [7,10] and theoretical models [11,13] evidence that the

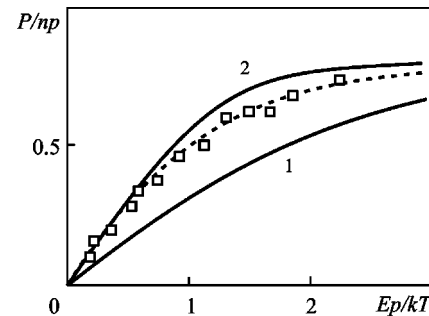


FIG. 5. Polarization density of the Stockmayer fluid. Points represent the computer calculations [8]; solid curves: 1, the Langevin law; 2, the first order perturbation model (10); dashed curve represents the modified mean-field model (32).

magnetostatic properties of ferrocolloids are described well while operating with the only parameter—the Langevin susceptibility χ_L . It means that the magnetic properties of ferrofluids are influenced only by the dipole-dipole correlations. This disagreement is convenient to study the basis of a monodisperse ferrofluid model, when the particle magnetic moment, concentration, and central interparticle interaction have to be considered as the independent parameters.

The central potential U_s is defined by the method of stabilization of a ferrocolloid. The use of surfactant layers in neutral liquids (for example, liquid hydrocarbons and magnetite particles stabilized by oleic acid) reveals that the U_s potential includes the steric repulsion and the van der Waals attraction. The ionic ferrofluids [24] are stabilized with the double electric layer mechanism. So, the U_s potential must include the electrostatic repulsion and van der Waals attraction. The interparticle interaction in ionic ferrofluids has been studied carefully in Ref. [25].

With the order of accuracy of expressions (24) and (25) the initial susceptibility of magnetic fluids is written as follows:

$$\chi = \chi_L \left\{ 1 + \frac{4\pi\chi_L}{3} \left[1 + \frac{m^4}{25(kT)^2} I \right] + \frac{(4\pi\chi_L)^2}{144} \right\}, \quad (26)$$

$$I = 6 \int_0^\infty \frac{\exp[-\beta U_s(r)]}{r^7} dr.$$

Here, the parameter I takes into account the central part of pair interparticle correlations. On the basis of this equation we have tested a lot of sterical and ionic stabilized model ferrocolloids at room temperatures in the range of parameters: the saturation magnetization of ferromagnetic material $M_s = 480$ kA/m (magnetite); the magnetic core diameter $x = 8 - 13$ nm; the concentration of magnetic phase φ_m up to 20%; the particle surface nonmagnetic layer thickness 0.5–0.8 nm; the Hamaker constant 2×10^{-19} to 4×10^{-19} J (hydrocarbons) and 2×10^{-20} to 4×10^{-20} J (water-based ferrofluids); the steric layer thickness 2–2.5 nm; the particle surface electrostatic potential $(4-5)kT$; the Debye electrostatic screening length $\kappa_D = 10-20d^{-1}$. Our calculations have shown the negligible difference between the cases of sterical and ionic stabilizations, but the computer data are dependent on the particle sizes. The typical results are plotted on Fig. 6 as the ferrofluid initial susceptibility vs the Langevin susceptibility for the magnetic core diameters $x = 10$ nm [Fig. 6(a)] and 13 nm [Fig. 6(b)]. The calculated data [expression (26)] are presented by points, the solid curves correspond to expression (20) and dashed curves represent the predictions of the 1st order perturbation model (10). For the magnetic core diameters x less than 11 nm we have not found any visible deviations between expressions (20) and (26) both for the sterical and for the ionic stabilized suspensions. For larger values $x \sim 12-15$ nm the small deviations appear ($\sim 5\%$) in the region $4\pi\chi_L \sim 7-8$ (magnetic phase concentration $\sim 15-20\%$). But the point is that in real polydisperse magnetic fluids the main number of ferro-particles are small in size $x = 7-10$ nm, and only the very

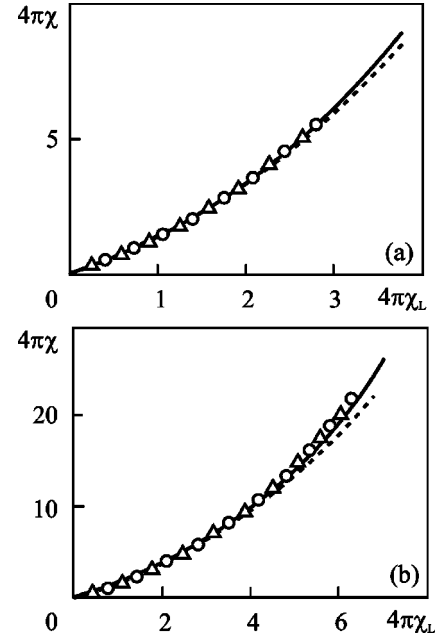


FIG. 6. Initial susceptibility of the model ferrofluids with the magnetic core diameters 10 nm (a) and 13 nm (b). Points represent the calculated data with the help of expression (26) for the sterical (\circ) and ionic (\triangle) stabilized systems. Solid curves represent the expression (20); dashed curves represent the expression (10).

small mole portion ($\sim 5-10\%$) of particles reaches the values $x \sim 12-15$ nm. That is why the deviation region [big particles, $4\pi\chi_L \sim 7-8$, Fig. 6(b)] is never realized in practically used magnetic colloids with the moderate concentrations of a magnetic phase. In this case, the universal expression (20) is valid for ferrofluids while using the polydisperse defined Langevin susceptibility $\chi_L = n\langle m^2 \rangle / 3kT$. The predictions of the first order perturbation model [13] and the modified mean-field model [10] in a form of expression (10) give the adequate description only for the moderately concentrated ferrofluids with the magnetic phase concentration $\varphi_m \sim 10\%$ and $4\pi\chi_L \sim 3$.

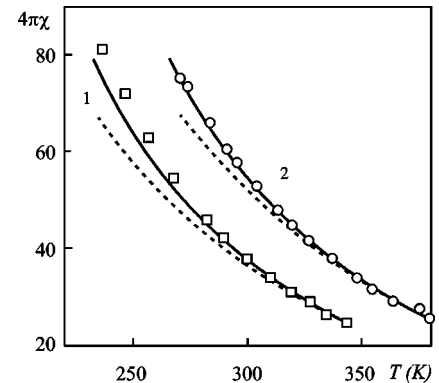


FIG. 7. Temperature dependence of the initial magnetic susceptibility of dense ferrofluids. Points represent the experimental data [17] (\diamond) and [7] (\circ). Solid curves 1 and 2 represent the expression (20); dashed curves 1 and 2 represent the expression (10).

The application of expression (20) to the temperature dependence of the initial susceptibility of dense ferrofluids ($\varphi_m \approx 18\%$) is shown in Fig. 7. These systems represent the dispersions of the so-called “drop-like aggregates,” arising during the phase separation of ferrocolloids. The droplets are highly concentrated and are enriched with the large particle fractions. The mean magnetic moment amounts up to $\langle m \rangle \sim 20 \times 10^{-19} \text{ A m}^2$. At low temperatures the susceptibility may be as great as $4\pi\chi \sim 80$. The adequate interpretation of $\chi(T)$ curves needs to take into account the following: the Langevin susceptibility decreases with increasing temperature not only due to the factor $1/T$ but also because of the liquid heat expansion (the number particle density decreases) and of the decreasing magnetization M_s of the particle material. The calculation procedure of such an account was described in Ref. [7]. In view of the above considerations the theoretical curves $\chi(T)$ in Fig. 7 were constructed in three stages: (i) calculation of the Langevin susceptibility $\chi_L(T_0)$ using the formula (20) and the experimental value of $\chi(T_0)$ at the reference temperature $T_0 = 345 \text{ K}$ (curve 1) and 380 K (curve 2); (ii) derivation of $\chi_L(T)$ at an arbitrary temperature accounting for the liquid heat expansion and temperature dependence of the magnetization M_s ; (iii) calculation of the initial susceptibility $\chi(T)$ in the framework of the presented theoretical model [expression (20)], and a comparison of the predicted and experimental values. The fact is that the presented model for the first time shows the good agreement with the experimental data [7,17]. So, the term proportional $\sim \chi_L^3$ in expression (20) is very important for the dense ferrofluids at low temperatures (see the solid and dashed curves on Fig. 7).

VI. MAGNETIZATION CURVES AND MODIFIED MEAN-FIELD THEORY

Applying to the magnetization curves of real ferrofluids the general method of Sec. II should be extended to the poly-disperse systems. Introducing the discrete ferroparticle distribution by size, we find, according to Eqs. (4) and (6),

$$M(H) = n \sum_k \nu_k m_k \frac{1}{2} \int_0^\pi \cos \omega_1 g_1^k(\omega_1) \sin \omega_1 d\omega_1, \quad (27)$$

$$\begin{aligned} \frac{dg_1^k(\omega_1)}{d\omega_1} &= -\alpha_k \sin \omega_1 g_1^k(\omega_1) - \frac{n}{kT} \sum_l \nu_l \int d\Omega_2 \\ &\times \int d\mathbf{r}_2 \frac{dU_d^{kl}(12)}{d\omega_1} g_2^{kl}(12). \end{aligned} \quad (28)$$

Here, ν_k stands for the mole portion of the particles of k fraction (magnetic moment m_k), and the particles 1 and 2 belongs to fractions k and l , respectively (upper indexes of the dipole-dipole potential and correlation functions). The summations over k and l correspond to the averaging over all the ferroparticle distribution by size.

The solution of equation (28), substituting in expression (27), leads to the following:

$$\begin{aligned} M(H) &= M_L(H) + \frac{n^2}{kT} \sum_{k,l} \nu_k \nu_l m_k \Omega_1^k \Omega_2^l [\cos \omega_1 - L(\alpha_k)] \\ &\times \int d(\cos \omega_1) \int d\mathbf{r}_{12} \frac{dU_d^{kl}(12)}{\sin \omega_1 d\omega_1} \tilde{g}_2^{kl}(12), \\ M_L(H) &= n \sum_k \nu_k m_k L(\alpha_k), \quad \alpha_k = \frac{m_k H}{kT}. \end{aligned} \quad (29)$$

Determination of the pair correlation function $\tilde{g}_2^{kl}(12)$ linear in dipole-dipole potential (Sec. III) gives the very cumbersome expression for the ferrofluid magnetization, containing a lot of terms. The main contribution is made by the three of them:

$$\begin{aligned} M(H) &= M_L(H) \left[1 + \frac{4\pi}{3} \frac{dM_L(H)}{dH} \right. \\ &+ \frac{1}{2} \left(\frac{4\pi}{3} \right)^2 M_L(H) \frac{d^2 M_L(H)}{dH^2} \\ &\left. + \frac{(4\pi)^2}{144} \left(\frac{dM_L(H)}{dH} \right)^2 + \dots \right]. \end{aligned} \quad (30)$$

Here, all the terms omitted do not make any contribution to the initial susceptibility. This expression represents the very complicated expansion of the ferrofluid magnetization M over the various combinations of the Langevin magnetization M_L and its derivatives. The first two terms in square brackets coincide with the result of the first order perturbation model (10).

The idea of approximation of the ferrofluid magnetization M in terms of the Langevin one M_L belongs to the modified mean-field model [10], which was discussed in the Introduction:

$$M(H) = M_L(H_e) = M_L[H + (4\pi/3)M_L(H)]. \quad (31)$$

The point is that the expansion of this expression with the accuracy $\sim (nm^2)^2 \sim (nU_d)^2$ gives the first three terms presented in expression (30). Evidently, the higher terms of such expansion $\sim (nU_d)^k$, $k = 3, 4, \dots$ will appear in the higher orders of the perturbation method. In other words, the developed statistical theory justifies the validity of the modified mean-field approach. However, the definition of an effective field H_e , according to Ref. [10] and expression (31), is insufficient for dense ferrofluids, especially for a weak magnetic field. But, on the basis of a success of approach (31) for moderately concentrated ferrocolloids we are able to suggest some modification, including the last term in expression (30),

$$M(H) = M_L(H_e) = n \int_0^\infty m(x) f(x) L \left[\frac{m(x) H_e}{kT} \right] dx, \quad (32)$$

TABLE I. Parameters of ferrofluids, magnetization curves of which are presented in Fig. 8. The fractional distributions by size were determined on the basis of results of Sec. VI.

| M_∞ (kA/m) | $n, 10^{22}$ (m^{-3}) | a | x_0 (nm) | $4\pi\chi_L$ | $4\pi\chi$ | $\langle m \rangle, 10^{-19}$ (A m) ² | $\langle x \rangle$ (nm) | Curve in Fig. 8 |
|----------------------|------------------------------|------|---------------|--------------|------------|---|-----------------------------|--------------------|
| 87.1 | 43.8 | 7.54 | 0.97 | 4.05 | 10.0 | 1.99 | 8.3 | 1 |
| 88.6 | 42 | 2.72 | 2.03 | 8.67 | 38.3 | 2.1 | 7.55 | 2 |

$$H_e = H + \frac{4\pi}{3} M_L(H) + \frac{(4\pi)^2}{144} M_L(H) \frac{dM_L(H)}{dH},$$

$$M(H) = \chi H, \quad \chi = \chi_L \left[1 + \frac{4\pi\chi_L}{3} + \frac{(4\pi\chi_L)^2}{144} \right], \quad H \rightarrow 0, \quad (33)$$

$$M(H) = \left(M_\infty - \frac{n k T}{H} \right) \left(1 + \frac{4\pi}{3} \frac{n k T}{H^2} \right), \quad H \rightarrow \infty. \quad (34)$$

Here, the additional term in the effective field H_e is proportional to the derivative of the Langevin magnetization, and results in the additional term in magnetic susceptibility. The asymptotics of the weak magnetic fields (33) coincide with the expression (20), and the asymptotics of the strong magnetic fields (34) correspond with the first order perturbation model [13]. The function $f(x)$ stands for the continuous ferroparticle distribution density by the magnetic core diameters.

We have tested the model (32) on the experimental magnetization curves [12,17] for the ferrofluids with the saturation magnetization $M_\infty = 87.1$ and 88.6 kA/m. The particle polydispersity was described by the gamma distribution,

$$f(x) = \frac{1}{x_0} \left(\frac{x}{x_0} \right)^a \frac{\exp(-x/x_0)}{\Gamma(a+1)}, \quad (35)$$

where x_0 and a are the parameters of the distribution density, and $\Gamma(z)$ stands for the gamma function. The magnetization curves were calculated in four stages according to the magnetogrulometric algorithm: (i) with the help of the strong field asymptotics (34) the fitting of the experimental data gives us the particle number density n and the mean magnetic moment $M_\infty = n \langle m \rangle$; (ii) the weak field asymptotics (33) allows us to obtain the Langevin susceptibility and,

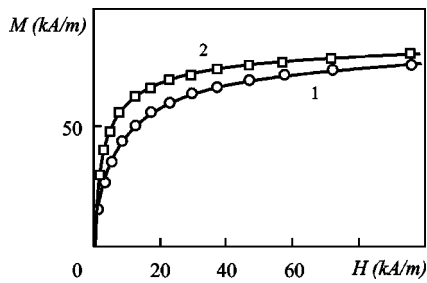


FIG. 8. Magnetization curves of dense ferrofluids. Points represent the experimental data [12] (\circ and 1) and [17] (\diamond and 2); curves represent the modified mean-field model (32).

hence, the mean squared magnetic moment $\langle m^2 \rangle$; (iii) since $\langle m \rangle \sim \langle x^3 \rangle$ and $\langle m^2 \rangle \sim \langle x^6 \rangle$, we are able to find the distribution parameters x_0 and a , which are presented in Table I; (iii) as a result, we calculate the ferrofluid magnetization (32) in the arbitrary values of an external field. The comparison, presented in Fig. 8, shows a very accurate agreement between the developed model (32) and the experimental data. Besides that, the expressions (32)–(35) allow us to determine the ferrofluid fractional distribution by the particle size (Fig. 9), which is of great importance for many applications.

It should be noted that the saturation magnetizations M_∞ of both ferrofluids are close, but the initial susceptibilities differ by the four times (Table I). The reason is that the ferrofluid 2 contains a number of big particles (Fig. 9), magnetic moments of which are greatly correlated. The latter leads to a faster increase of magnetization 2 in the weak magnetic fields as compared with magnetization 1 (curves 1 and 2, Fig. 8).

VII. CONCLUSION

With the help of the BBGKI method the ferrofluid magnetization was expressed in terms of the pair correlation function of the ferroparticle system. This new approach allows us to develop the cluster expansion of the ferrofluid magnetization (polar fluid polarization) over both the particle concentration n and the interparticle dipole-dipole interaction U_d in an arbitrary valued external field. An important advantage of the method is that the determination of the pair correlation function up to the order of $\sim n^k, U_d^k$ gives the magnetization in terms of the order $\sim n^{k+1}, U_d^{k+1}$.

The exact expressions for the ferrofluid initial magnetic susceptibility and the polar fluid dielectric constant were obtained under the condition that the interparticle dipole-dipole correlations linear in U_d have been taken into account. We

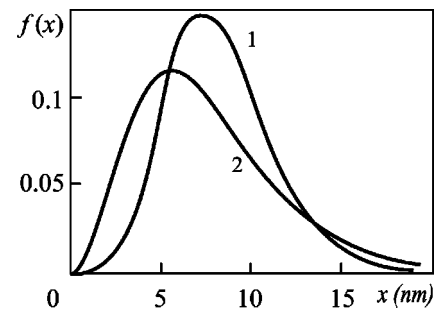


FIG. 9. Ferroparticle distribution density by the magnetic core diameters. Curves correspond to the ferrofluids 1 and 2 (Fig. 8).

have shown that the result of the Weiss mean-field model will appear while neglecting the presence of excluded volumes for interacting particles due to the central interparticle interaction. The obtained expressions for the dielectric constant of both the dipolar hard sphere fluid and the Stockmayer fluid were compared with the known computer calculations. Our results describe well the data of computer modeling and substantiate that the dielectric properties of dense polar fluids are influenced not only by the dipole-dipole interaction but the central interparticle correlations as well.

Applying our results to dense ferrocolloids we have studied the dependence of the initial magnetic susceptibility on the stabilization method of a magnetic suspension; this dependence was shown to be very weak for real ferrofluids. This conclusion justifies the validity of the obtained expression for the initial susceptibility in a form of the expansion over the universal parameter—the Langevin susceptibility. The theory presented gives the accurate description of the temperature dependence of the magnetic susceptibility for dense ferrofluids. The magnetization was studied in terms of the second order perturbation method over the dipole-dipole interaction energy. We have justified the validity of the modified mean-field approach and have suggested the statis-

tical method of determination of the effective field, acting on a single particle. The obtained expression for magnetization allows us to determine the correct fractional contents and describes very accurately the total magnetization curves even for ferrofluids with the maximum allowable concentration of a magnetic phase $\sim 18\%$. This is caused by the fact that our result is expressed on the basis of the modified mean-field model. We have shown that such an approach represents a special form of perturbation theory, when the ferrofluid magnetization is evaluated as an expansion over the Langevin magnetization. The explicit form of this expansion is controlled by the pair correlations of ferroparticle magnetic moments.

ACKNOWLEDGMENTS

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APPENDIX A

Calculating the derivatives in expression (3), we get

$$\begin{aligned}
 M &= -\frac{1}{V} \frac{\partial}{\partial H} (-kT \ln \tilde{Q}) \\
 &= \frac{kT}{V} \frac{\partial}{\partial H} \left\{ \ln \left[\left(\frac{\sinh \alpha}{\alpha} \right)^N Q \right] \right\} \\
 &= \frac{kT}{V \tilde{Q}} \frac{\partial}{\partial H} \prod_{i=1}^N \hat{R}_i \prod_{i=1}^N \int d\Omega_i \exp(-\beta \hat{H}_m - \beta \hat{H}_s - \beta \hat{H}_d) \\
 &= \frac{kT}{V \tilde{Q}} \prod_{i=1}^N \hat{R}_i \prod_{i=1}^N \int d\Omega_i \exp(-\beta \hat{H}_m - \beta \hat{H}_s - \beta \hat{H}_d) \frac{m}{kT} \sum_{i=1}^N \cos \omega_i \\
 &= \frac{nm}{Q} \hat{R}_1 \int d\Omega_1 \left(\frac{\alpha}{\sinh \alpha} \right) \exp(\alpha \cos \omega_1) \cos \omega_1 \prod_{i=2}^N \hat{R}_i \prod_{i=2}^N \int \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d) \\
 &= nm \hat{R}_1 \int d\Omega_1 \cos \omega_1 g_1(r_1, \Omega_1).
 \end{aligned}$$

Here we define the one-particle distribution function as the Gibbs distribution averaging over the coordinates and orientations of all particles except one according to

$$g_1(\mathbf{r}_1, \Omega_1) = \left(\frac{\alpha}{\sinh \alpha} \right) \frac{\exp(\alpha \cos \omega_1)}{Q} \prod_{i=2}^N \hat{R}_i \prod_{i=2}^N \int \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d).$$

Assuming that for a homogeneous ferrofluid the function g_1 does not depend on \mathbf{r}_1 and ζ_1 , we come to the expression

$$M = nm \frac{1}{2} \int_0^\pi \cos \omega_1 g_1(\omega_1) \sin \omega_1 d\omega_1.$$

APPENDIX B

Let us calculate the derivative of the function $g_1(\omega_1)$ with respect to the angle variable ω_1 :

$$\begin{aligned}
\frac{dg_1(\omega_1)}{d\omega_1} &= \frac{d}{d\omega_1} \left(\frac{\alpha}{\sinh \alpha} \right) \frac{\exp(\alpha \cos \omega_1)}{Q} \prod_{i=2}^N \hat{R}_i \prod_{i=2}^N \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d) \\
&= -\alpha \sin \omega_1 \left(\frac{\alpha}{\sinh \alpha} \right) \frac{\exp(\alpha \cos \omega_1)}{Q} \prod_{i=2}^N \hat{R}_i \prod_{i=2}^N \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d) \\
&\quad + \left(\frac{\alpha}{\sinh \alpha} \right) \frac{\exp(\alpha \cos \omega_1)}{Q} \prod_{i=2}^N \hat{R}_i \prod_{i=2}^N \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d) \frac{d}{d\omega_1} \sum_{j=2}^N \left[-\frac{U_d(1j)}{kT} \right] \\
&= -\alpha \sin \omega_1 g_1(\omega_1) - \frac{N-1}{kT} \left(\frac{\alpha}{\sinh \alpha} \right) \frac{\exp(\alpha \cos \omega_1)}{Q} \hat{R}_2 \hat{\Omega}_2 \frac{dU_d(12)}{d\omega_1} \prod_{i=3}^N \hat{R}_i \prod_{i=3}^N \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d) \\
&= -\alpha \sin \omega_1 g_1(\omega_1) - \frac{n}{kT} \int d\mathbf{r}_2 \int d\mathbf{\Omega}_2 \frac{dU_d(12)}{d\omega_1} g_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{\Omega}_1, \mathbf{\Omega}_2).
\end{aligned}$$

Here we define the pair correlation function g_2 as the Gibbs distribution averaging over the coordinates and orientations of all particles except two according to

$$\begin{aligned}
g_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{\Omega}_1, \mathbf{\Omega}_2) &\equiv g_2(12) = \left(\frac{\alpha}{\sinh \alpha} \right)^2 \frac{\exp[\alpha(\cos \omega_1 + \cos \omega_2)]}{Q} \prod_{i=3}^N \hat{R}_i \prod_{i=3}^N \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d) \\
&= \left(\frac{\alpha}{\sinh \alpha} \right)^2 \exp[\alpha(\cos \omega_1 + \cos \omega_2)] \tilde{g}_2(12), \\
\tilde{g}_2(12) &= \prod_{i=3}^N \hat{R}_i \prod_{i=3}^N \hat{\Omega}_i \exp(-\beta \hat{H}_s - \beta \hat{H}_d) / Q.
\end{aligned}$$

The function $\tilde{g}_2(12)$ has the meaning of the pair correlation function $g_2(12)$, separating out the one-particle distribution functions of an ideal paramagnetic gas (5): $(\alpha/\sinh \alpha) \exp(\alpha \cos \omega_i), i=1,2$.

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