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Dynamical susceptibility of solid ferrocolloids

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A theoretical analysis of the dynamical magnetic susceptibility of a frozen nondilute ferrocolloid is presented. The steric and dipole-dipole interactions between ferroparticles are taken into account. Two systems are studied. The first is the homogeneous solid ferrocolloid with separate individual particles. The second is a ferrocolloid with heterogeneous chainlike aggregates. The effect of the magnetodipole interparticle interaction on the real and imaginary parts of the dynamical susceptibilities of these systems is estimated.

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I. INTRODUCTION

The interest of investigators in systems of dipole particles embedded in a solid matrix has increased in recent years (see, for example, Refs. [1–8]). A ferrocolloid (magnetic liquid) in a frozen solvent is an example of such a system. As soon as the solvent is frozen, both the space arrangement of the ferromagnetic particles and the orientations of their axes of easy magnetization become fixed. Thus, the static and dynamical magnetic susceptibilities of such systems may differ essentially from those of ferrocolloids in solvents in a liquid state.

The initial susceptibilities of very dilute solid ferrocolloids were studied in [4,5]. An analysis of the susceptibility of moderately concentrated colloids taking into account the magnetodipole interaction between particles was performed in Ref. [9]. Those calculations were made under the assumption that the magnetic interparticle interaction is small or moderate, and the external field is weak. However, experiments [6–8] demonstrate that in many real solid ferrocolloids these interactions play a very important role in the macroscopic response to an external field. In the view of the authors of [6–8], the results of their experiments suggest a dipole-glass state of the systems under study. However, various heterogeneous aggregates (for example, chainlike, droplike, etc.) can arise in the colloid if the magnetic interparticle interaction is strong before freezing. The effect of these aggregates on the macroscopic properties of solid ferrocolloids is not understood theoretically. To study this effect is one of the aims of our work. Below it is shown that the presence of chainlike aggregates can induce effects similar to those in a dipole-glass state.

As mentioned above, previously the dynamical susceptibilities of solid ferrocolloids have been studied theoretically only for a very weak external field. However, the magnetic field acting on the colloid is often not weak and thus account must be taken of the influence of the field on the dynamical response functions of the colloid. The second aim of this work is to derive the nonlinear response functions to moderate magnetic fields of homogeneous moderately concentrated ferrocolloids.

Consider a system of N identical spherical single-domain particles. The absolute value m of the magnetic moment of a particle is constant. The colloid becomes frozen instantaneously; therefore the space arrangement of the particles and the orientation of their axes of light magnetization after freezing remain as before.

II. HOMOGENEOUS FERROCOLLOIDS

The initial susceptibility of ferrocolloids solidified in a magnetic field arbitrary in both magnitude and direction have been studied in Ref. [9]. In this part of the article we focus our attention on systems frozen in a high magnetic field. For this reason the easy axes of magnetization of all particles in the solid colloid are aligned along the field. We suppose that the current magnetic field has the same direction.

Let $\mathbf{e}_i$ be the unit vector aligned along the magnetic moment $\mathbf{m}_i$ of the ith particle, and $f_1(\mathbf{e})$ the one-particle distribution function normalized to unity. The macroscopic magnetization of the colloid is

$$\mathbf{M}=mc\langle\mathbf{e}\rangle, \qquad \langle\mathbf{e}\rangle=\int \mathbf{e}f_1(\mathbf{e})d\mathbf{e}, \tag{1}$$

where c is the number of particles in unit volume of the colloid.

The distribution function f_1 can be derived using the Fokker-Planck equation,

$$\frac{\partial f_1}{\partial t}=\zeta\mathbf{J}(f_1\mathbf{J}u_1)+\zeta\mathbf{J}(f_1\mathbf{J}u_2)+D\mathbf{J}^2f_1,$$

$$u_1(\mathbf{e})=-T(\alpha\mathbf{e})+u_a, \quad u_2(\mathbf{e})=NU(\mathbf{e}), \tag{2}$$

$$\alpha=\frac{m\mathbf{H}}{T}, \quad D=\zeta T, \quad \mathbf{J}=\left[\mathbf{e},\frac{\partial}{\partial\mathbf{e}}\right].$$

Here ζ is a kinetic coefficient, T is the absolute temperature in energy units, $\mathbf{H}$ is the external magnetic field, $u_a(\mathbf{e})$ and $u_1(\mathbf{e})$ are the energy of magnetic anisotropy of a particle and the total energy of a particle in the field $\mathbf{H}$, and $U(\mathbf{e})$ is the mean energy of dipole-dipole interaction of a given particle with the others.

Directing the axis Oz along the current magnetic field (and, therefore, along the easy axis of magnetization of the particle) and using the well-known approximation for u_a, we can write

$$u_a = -Ke_z^2, \tag{3}$$

where K is the coefficient of magnetic anisotropy of the particle. By definition

$$U(\mathbf{e}) = \int w(\mathbf{e},\mathbf{e}_1,\mathbf{r}) f_2(\mathbf{e}_1,\mathbf{r}|\mathbf{e}) d\mathbf{e}_1 d\mathbf{r}. \tag{4}$$

Here w is the dipole-dipole interaction potential of two particles with orientation vectors $\mathbf{e}$ and $\mathbf{e}_1$, $\mathbf{r}$ is the radius vector connecting them, and f_2 is the conditional binary distribution function. In order to determine f_2 we need to formulate a two-particle Fokker-Planck equation, which involves a three-particle equation, etc.

Here, as in Ref. [9], we assume the interparticle interaction to be moderate or weak. Therefore, in the first approximation for this interaction we come to

$$f_2(\mathbf{e}_1,\mathbf{r}|\mathbf{e}) = \frac{1}{V} p(\mathbf{e}_1), \quad r > 2a,$$
$$f_2 = 0, \quad r < 2a, \tag{5}$$

where a is the radius of the particle, V is the volume of the colloid, and p is the single-particle distribution function without the interparticle interaction. The last condition in Eq. (5) takes into account that the particles do not overlap.

The Fokker-Planck equation for p is

$$\frac{\partial p}{\partial t} = \zeta \mathbf{J}(p\mathbf{J}u_1) + D\mathbf{J}^2 p. \tag{6}$$

The exact solution of this equation is unknown. Here we consider particles with a large magnetic anisotropy for which the strong inequalities $\sigma = K/T \gg 1$, $\sigma \gg \alpha$ hold good.

Since $\sigma \gg 1$, the probabilities for the particles to be in states $e_z = \pm 1$ are much greater than those for other states. Therefore in the first approximation of the small parameter $1/\sigma$ we can write

$$p(\mathbf{e},t) = n_+(t)\delta(e_z - 1) + n_-(t)\delta(e_z + 1),$$
$$n_+(t) + n_-(t) = 1, \tag{7}$$

where $\delta(x)$ is the delta function and $n_\pm$ are probabilities for the particle to be in states $e_z = \pm 1$, respectively.

Repeating the reasoning of Ref. [5], and taking into account that $\alpha \ll \sigma$, we arrive at the relations

$$n_\pm(t) = \frac{1}{q(t)}\left[n_\pm(0)q(0) + \int_0^t W_\mp(s)q(s)ds \right],$$
$$q(t) = \exp\left(\int_0^t [W_+(s) + W_-(s)]ds \right), \tag{8}$$
$$W_\pm = C_\pm \exp[-(\sigma \pm \alpha)],$$
$$C_\pm = \zeta T(\pm\alpha + 2\sigma)\left(\frac{\sigma}{\pi}\right)^{1/2}.$$

Substituting Eq. (7) into Eq. (5) and then into Eq. (4), after calculations described in Ref. [9], we get

$$U = -\frac{v}{V} 8\gamma e_{1z}[n_+(t) - n_-(t)],$$
$$v = \frac{4\pi}{3}a^3, \quad \gamma = \frac{m^2}{(2a)^3 T}. \tag{9}$$

The dimensionless parameter γ characterizes the ratio of the energy of the dipole-dipole interaction of two closely spaced particles to the thermal energy of the system.

Inserting Eq. (7) into the second relation of Eq. (3) and then into Eq. (2), taking into account that now $(\alpha\mathbf{e}) = \alpha e_z$, one can rewrite Eq. (2) as follows:

$$\frac{\partial f_1}{\partial t} = \zeta \mathbf{J}(f_1 \mathbf{J} u_{1e}) + D\mathbf{J}^2 f_1,$$
$$u_{1e} = -(\alpha_e \mathbf{e}) + u_a, \tag{10}$$
$$\alpha_e(t) = \alpha(t) + 8\rho\gamma[n_+(t) - n_-(t)].$$

Here $\rho = cv$ is the volume concentration of the particles. Equation (10) coincides formally with Eq. (6) with the effective dimensionless field α_e instead of the real field α.

Repeating arguments identical to those for Eq. (7), we can write

$$f_1(\mathbf{e},t) = q_+(t)\delta(e_z - 1) + q_-(t)\delta(e_z + 1), \quad q_+ + q_- = 1. \tag{11}$$

The expressions for $q_\pm$ can be obtained from Eq. (8) for $n_\pm$ by using the effective field α_e instead of α.

Substituting Eq. (11) into Eq. (1), we have

$$\langle e_z \rangle(t) = q_+(t) - q_-(t), \quad M(t) = m\frac{\rho}{v}\langle e_z \rangle(t). \tag{12}$$

Thus, in order to calculate the magnetization M we need, first, to determine $n_\pm$. Second, taking into account Eqs. (10) and (8), we derive $q_\pm$ (to do this, we replace $n_\pm$ by $q_\pm$ and α by α_e) and, finally, use relations (12).

III. NONLINEAR RESPONSE OF HOMOGENEOUS FERROCOLLOIDS TO AN OSCILLATING FIELD

The foregoing procedure can be realized numerically for arbitrary $\alpha(t)(\alpha\ll\sigma)$. Here we study the nonlinear response to a moderate or weak oscillating field,

$$\alpha(t)=\alpha_0\cos\omega t,\quad \alpha_0<1. \tag{13}$$

Neglecting terms of magnitude of the order of α_0/σ and less, using Eq. (8) we can easily obtain

$$W_+(s)+W_-(s)=\tau_0^{-1}\cosh\alpha(s),$$

$$W_+(s)-W_-(s)=\tau_0^{-1}\sinh\alpha(s), \tag{14}$$

$$\tau_0=\tau^o\frac{\exp(\sigma)}{\kappa^{1/2}},\quad \tau^o=\frac{\pi^{1/2}}{4\zeta K}.$$

In a quadratic approximation in α we get

$$\frac{q(s)}{q(t)}=\exp\left(\frac{1}{\tau_0}\int_t^s\cosh\alpha(y)dy\right)$$
$$=\exp\left(\frac{s-t}{\tau_0}\right)\left(1+\frac{1}{2\tau_0}\int_t^s\alpha^2(s)ds\right),$$

$$\int_0^t[W_-(s)-W_+(s)]ds$$
$$=\frac{\exp(-t/\tau_0)}{\tau_0}\int_0^t\exp\left(\frac{s}{\tau_0}\right)\alpha(s)$$
$$\times\left(1+\frac{1}{6}\alpha^2(s)+\frac{1}{2\tau}\int_t^s\alpha^2(y)dy\right), \tag{15}$$

$$n_+(t)-n_-(t)=[n_{+o}(t)-n_{-o}(t)]$$
$$\times\exp\left(-\frac{t}{\tau_0}\right)\left(1+\frac{1}{2\tau_0}\int_0^s\alpha^2(s)ds\right)$$
$$+\frac{\exp(-t/\tau_0)}{\tau_0}\int_0^t\exp\left(\frac{s}{\tau_0}\right)\alpha(s)$$
$$\times\left(1+\frac{1}{6}\alpha^2(s)+\frac{1}{2\tau_0}\int_t^s\alpha^2(y)dy\right),$$

where $n_{\pm o}$ are random initial values of $n_\pm$. Substituting Eq. (13) into Eq. (15), after simple but cumbersome calculations we have for $t\gg\tau$

$$n_+(t)-n_-(t)=\alpha_0(\beta_1'+\alpha_0^2\varphi')\cos\omega t+\alpha_0$$
$$\times(\beta_1''+\alpha_0^2\varphi'')\sin\omega t+\alpha_0^3\beta_2'\cos 3\omega t$$
$$+\alpha_0^3\beta_2''\sin 3\omega t,$$

$$\beta_1'=\frac{1}{1+(\omega\tau)^2},\quad \beta_1''=\frac{\omega\tau}{1+(\omega\tau)^2},$$

$$\varphi'=p_1\left[\left(p_2-\frac{1}{2}\beta_1'\right)p_3+\frac{1}{2}\frac{(\beta_1'')^2}{p_1}\right], \tag{16}$$

$$\varphi''=\omega\tau p_1\left[\left(p_2+\frac{1}{2}\beta_1'\right)p_3-\frac{1}{2}\frac{(\beta_1')^2}{p_1}\right],$$

$$\beta_2'=\beta_1'p_1\left(\frac{p_2}{4\beta_1'}+\frac{3}{8}(\omega\tau)^2\right),\quad \beta_2''=\beta_1''p_1\left(\frac{3}{4}p_2-\frac{1}{8}\right),$$

$$p_1=\frac{1}{1+9(\omega\tau)^2},\quad p_2=\frac{1}{6}-\frac{1}{4(1+(\omega\tau)^2)},$$

$$p_3=\frac{3}{4}+6\frac{(\omega\tau)^2}{1+(\omega\tau)^2}.$$

Substituting Eq. (16) into Eq. (9) and then into Eq. (10), and using α_e instead of α in Eq. (15), we determine q_+ and q_-. Having performed calculations in the cubic approximation in α_0 for $t\gg\tau_0$, we obtain

$$\langle e_z\rangle=\alpha_0(B_1'+\alpha_0^2\Phi')\cos\omega t+\alpha_0(B_1''+\alpha_0^2\Phi'')\sin\omega t$$
$$+\alpha_0^3B_2'\cos 3\omega t+\alpha_0^3B_2''\sin 3\omega t, \tag{17}$$

where

$$B_1'=\beta_1'+8\rho\gamma[(\beta_1')^2+L_1'],$$

$$B_1''=\beta_1''+8\rho\gamma(\beta_1'\beta_1''+L_1''),$$

$$\Phi'=\varphi'+8\rho\gamma(4\beta_1'\varphi_1'+L_2'),$$

$$\Phi''=\varphi''+8\rho\gamma(3\beta_1'\varphi'+\beta_1''\varphi_1'+L_2''),$$

$$B_2'=\beta_2'+8\rho\gamma\left(3\beta_1'\beta_2'+L_3'+\frac{\beta_2'-3\omega\tau\beta_2''}{1+(3\omega\tau)^2}\right),$$

$$B_2''=\beta_2''+8\rho\gamma\left(3\beta_1'\beta_2''+L_3''+\frac{\beta_2''+3\omega\tau\beta_1'}{1+(3\omega\tau)^2}\right),$$

$$L_1'=-(\beta_1'')^2,\quad L_1''=\beta_1'\beta_1'',$$

$$L_2'=\omega\tau\{[p_1p_3(\tfrac{1}{4}\beta_1'+p_2)-p_2\beta_1']-\varphi_1''\beta_1'\},$$

$$L_2''=\{p_1p_3[p_2+\tfrac{1}{4}(\omega\tau)^2\beta_1']+p_2\beta_1''\})+\beta_1'\varphi'',$$

$$L_3'=\omega\tau\frac{p_1\beta_1''}{4}\left(\frac{1}{4}\beta_1'-3p_2\right),$$

$$L_3''=\frac{p_1\beta_1''}{4}\left(\frac{3}{4}(\omega\tau)^2\beta_1'+p_2\right).$$

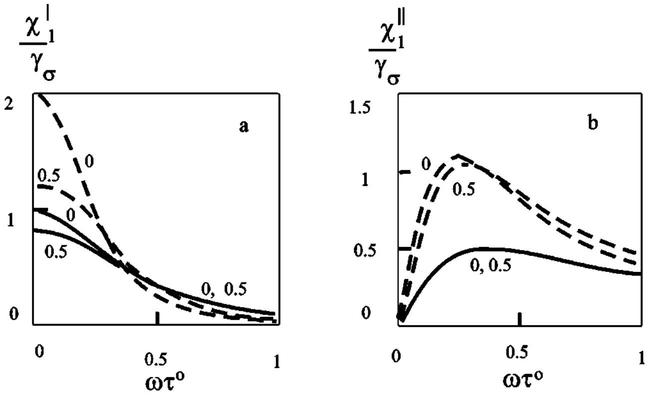

FIG. 1. Real (a) and imaginary (b) parts of the normalized dynamical susceptibility of a homogeneous ferrocolloid to the signal frequency ω vs this frequency when $\sigma=1$. Solid and dashed curves correspond to $\gamma=0$ and $8\pi\gamma\rho=1$, respectively. Figures near curves are values of α_0.

Let us expand the magnetization in a Fourier series,

$$M(t)=\sum_n \left[M_n' \cos(\omega nt)+M_n'' \sin(\omega nt)\right], \tag{18}$$

and denote

$$\chi_n'(\omega)=\frac{M_n'}{H_0}, \quad \chi_n''(\omega)=\frac{M_n''}{H_0}. \tag{19}$$

Equations (19) are the definitions of the nonlinear real χ_n' and imaginary χ_n'' parts of the dynamical response functions corresponding to the frequency $n\omega$ multiplied by the signal frequency ω. Using Eq. (17), we have

$$\begin{aligned}\chi_1'&=\sigma(B_1'+\alpha_0^2\Phi')\gamma_\sigma,\\ \chi_1''&=\sigma(B_1''+\alpha_0^2\Phi'')\gamma_\sigma,\\ \chi_3'&=\alpha_0^2\sigma B_2'\gamma_\sigma,\\ \chi_3''&=\alpha_0^2\sigma B_2''\gamma_\sigma,\\ \gamma_\sigma&=\frac{m^2n}{K}=\frac{6\rho\gamma}{\sigma}.\end{aligned} \tag{20}$$

The results of some calculations of χ_1' and χ_1'' are given in Figs. 1 and 2. Relations (20) and Figs. 1 and 2 allow us to draw the following conclusions. First, the initial ($\alpha_0\to 0$) response functions χ_1 corresponding to the signal frequency have the Debye form with the characteristic time τ_0 provided that the interparticle dipole-dipole interaction is negligible ($\rho\gamma\to 0$). If α_0 and (or) $\rho\gamma$ are not negligible, these response functions lose the Debye form. It should be stressed that this result is mathematically strict. It is also interesting to note that the initial susceptibility of a nondilute liquid ferrocolloid has the Debye form with the relaxation time depending on $\rho\gamma$ [10,11].

Second, the functions χ_3 corresponding to the response to the frequency 3ω lack the Debye form even in the absence of interparticle interaction. Our estimations show that if the field α is not large χ_3 are much less than χ_1.

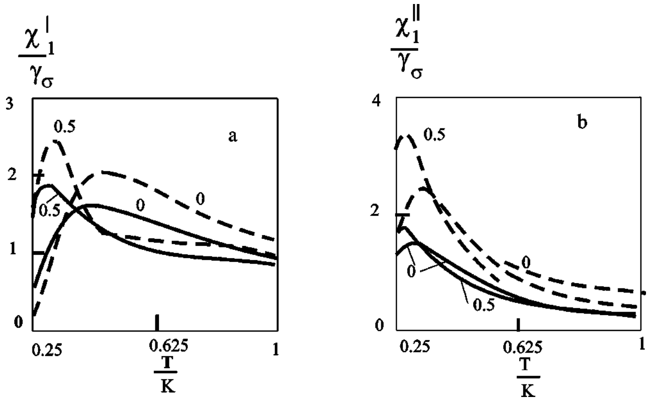

FIG. 2. Temperature dependence of the normalized components of the susceptibility of a homogeneous ferrocolloid on the signal frequency when $\omega\tau^0=0.1$. Solid and dashed curves correspond to $x=8\rho m^2/(vK)=0$ and 0.25, respectively. Figures near curves are values of dimensionless field amplitude $\alpha^0=\alpha_0/\sigma$.

Figure 1 shows that the interparticle interaction increases the response function χ_1' when ω is small enough. Such a result for the stationary susceptibility of liquid ferrocolloids is well known (see, for example, Refs. [10–13]). The imaginary part χ_1'' of the susceptibility to the signal frequency increases, whereas the frequency corresponding to the maximum of χ_1'' decreases when the product $\rho\gamma$ increases. This means that an increase of magnetic interparticle interaction in homogeneous ferrocolloids leads to an increase of the effective time of magnetic relaxation of these systems.

Figure 2 shows that the temperature dependences of χ_1' and χ_1'' have maxima. This conclusion is consistent with the results of experiments [1–3,6–8]. The temperatures of these maxima increases with increasing interparticle interaction. It should be noted that these maxima were interpreted in [2] as signs of a dipole-glass state in the solid ferrocolloid. However, they occur even in a single-particle approximation. Therefore, to explain the temperature maxima of χ it is not necessary to use the hypothesis of a dipole-glass state of the ferrocolloid.

IV. FERROCOLLOIDS WITH CHAINLIKE AGGREGATES: MODEL AND DISTRIBUTION FUNCTION OVER THE CHAIN SIZE

Let us consider an equilibrium liquid magnetic ferrocolloid with chainlike aggregates. Here we adopt the following assumptions. First, we assume that the volume concentration ρ of the particles is small and any interaction between particles in different chains may be neglected. Second, we treat the chains as straight aggregates consisting of contacting particles and ignore the fluctuations in their shape. The conditions of validity of this approximation will be determined further. Third, we suppose that the colloid was solidified rapidly and in the solid state it has the same inner structure as in the liquid state. Next, we assume that in the liquid state the dipole-dipole interaction between contacting particles is large and the inequalities $\gamma \gg \alpha, \gamma \gg 1$ hold good.

Treating the chains as heterogeneous fluctuations and using the well-known Frenkel theory [14] of such fluctuations, we represent the free energy per unit volume of the liquid ferrocolloid as follows:

$$F = T \sum_n \left[g_n \ln\left(\frac{g_n v}{e}\right) + g_n f_n \right]. \tag{21}$$

Here n is the number of particles in the chain, g_n is the number of n-particle chains in the unit volume, and f_n is the ''internal'' energy of the chain. The first term in brackets in Eq. (21) stands for the entropy of a gas of n-particle chains due to their translational motion.

In order to calculate f_n we use the nearest-neighbor approximation, taking into account the dipole-dipole interaction only between directly adjacent particles in the chain. Simple estimates show that for an unlimited straight chain the relative error of this approximation is less than 20%. For short chains the error is smaller.

Because the dipole-dipole interaction parameter γ is large, one can suppose that the magnetic moments of all particles are aligned in one direction—along the chain axis. Therefore, the n-particle chain can be represented as a straight aggregate with the magnetic moment mn directed along the axis of this aggregate.

The dimensionless free energy of interaction of this aggregate with the magnetic field is

$$f_m = -\ln \frac{\sinh(\alpha n)}{\alpha n}.$$

In the nearest-neighbor approximation the dimensionless energy of the dipole-dipole interactions of all particles in the chain is

$$f_d = -2\gamma(n-1).$$

The total internal free energy is

$$f_n = f_m + f_d = -\left(\ln \frac{\sinh(\alpha n)}{\alpha n} + 2\gamma(n-1) \right). \tag{22}$$

It should be noted that it is not difficult to estimate f_d without the nearest-neighbor approximations, taking into account the magnetodipole interactions of all particles in the chain. The results obtained are quantitatively close to ours, but the relations for f_d and f_n become very cumbersome. For this reason we use the simple and physically adequate approximation (22).

At equilibrium the distribution function g_n should minimize F under the normalization condition

$$\sum_n n g_n = \frac{\rho}{v}. \tag{23}$$

After calculations we have

$$g_n = \frac{x^n}{v} \frac{\sinh(\alpha n)}{\alpha n} \exp(-2\gamma), \tag{24}$$

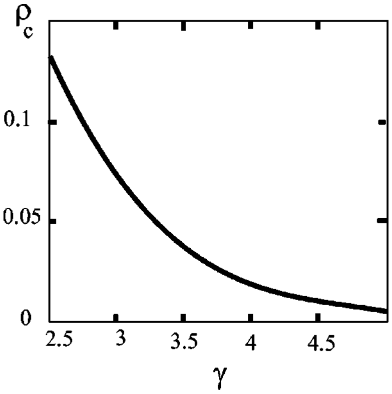

FIG. 3. Critical volume concentration ρ_c of ferroparticles for the model of straight chain aggregates, as a function of the dimensionless interparticle interaction parameter γ_0, which is the value of γ at the temperature of solidification.

where

$$x = \frac{2y \cosh\alpha + \sinh\alpha - \sqrt{(2y\cosh\alpha + \sinh\alpha)^2 - 4y^2}}{2y},$$

$$y = \alpha\rho \exp(2\gamma). \tag{25}$$

The mean number of particles in the chain is

$$\langle n \rangle = \frac{\sum_n n g_n}{\sum_n g_n} = \frac{\alpha\rho \exp(2\gamma)}{\sum_n [x^n \sinh(\alpha n)/n]}. \tag{26}$$

Using well-known results from the theory of polymer chains, one get the estimate $l \sim 2d\gamma$ for the persistent length l of the chain. Thermal fluctuations in shape for such a situation are small and therefore the chain can be treated as a straight rod. If $l > d\langle n \rangle$, this approximation is acceptable for the ensemble of chains. Thus we can use the following criterion for the model of the chains as straight aggregates:

$$\langle n \rangle < 2\gamma.$$

Let us denote by ρ_c the particle volume concentration for which $\langle n \rangle = 2\gamma$. If $\rho < \rho_c$, then $\langle n \rangle < 2\gamma$ and the model can be used. The results of calculations of ρ_c for zero field are shown in Fig. 3.

V. HIGH-FREQUENCY SUSCEPTIBILITY OF SOLID FERROCOLLOIDS WITH CHAINS

Let us consider an n-particle straight chain directed at the angle θ to the external field. Let the strong inequalities $\sigma \gg 1 \gg \alpha$ hold good. Because in the liquid state of the colloid, when the chains are formed, the energies of both interparticle interaction and magnetic anisotropy of the particles are large, we can suppose that the easy axes of magnetization of all particles in the chain are aligned along the chain axis.

In the framework of accepted approximations the energy of one particle in the chain is

$$\varepsilon(\mathbf{e}) = -\left[m(\mathbf{e}\cdot\mathbf{H}) + K(\mathbf{e}\nu)^2 + \sum_j \frac{m^2}{(2a)^3 j^3} \times [3(\mathbf{e}\xi_j)(\mathbf{e}_j\xi_j) - (\mathbf{e}\cdot\mathbf{e}_j)] \right],$$

$$\mathbf{e} = \frac{\mathbf{m}}{m}, \quad \mathbf{e}_j = \frac{\mathbf{m}_j}{m}, \quad m = |\mathbf{m}| = |\mathbf{m}_j| = \text{const.} \tag{27}$$

Here $\mathbf{m}$ and $\mathbf{m}_j$ are the magnetic moments of a given and the jth particle in the chain, respectively, ξ is the unit vector directed from the center of the given particle to the center of the jth particle, and $\boldsymbol{\nu}$ is the unit vector aligned along the easy axis of magnetization of the particle. The summation is performed over all particles in the chain except the one under consideration.

Because the energy of magnetic anisotropy of the particle is large, two deep potential pits arise corresponding to orientation of the particle magnetic moment along and opposite to vector ν. Hence, as above, the orientation distribution function $\varphi(\mathbf{e})$ can be written as

$$\varphi(\mathbf{e}) = p_+\delta(\mathbf{e}-\boldsymbol{\nu}) + p_-\delta(\mathbf{e}+\boldsymbol{\nu}), \quad p_+ + p_- = 1, \tag{28}$$

where $p_\pm$ are the probabilities for the particle to be in states $\mathbf{e} = \pm\boldsymbol{\nu}$, respectively.

These probabilities can be determined using the appropriate Fokker-Planck equation for the given particle. This equation includes the energy ε. Because of the dipole-dipole interaction term in Eq. (27), this one-particle Fokker-Planck equation involves a similar two-particle equation, and so on.

In order to break this chain of equations and to get a constructive approximate solution, let us average Eq. (27) over all orientations of the moments of all particles in the chain except the one under consideration. After this averaging Eq. (27) can be rewritten as

$$\varepsilon = -T\left[(\mathbf{e}\alpha) + \sigma(\mathbf{e}\alpha)^2 + \gamma\sum_j \frac{1}{j^3}[3(\mathbf{e}\xi_j)(\mu_n\xi_j) - (\mathbf{e}\mu_n)] \right],$$

$$\boldsymbol{\alpha} = \frac{m\mathbf{H}}{T}, \quad \sigma = \frac{K}{T}, \quad \gamma = \frac{m^2}{(2a)^3 T}, \tag{29}$$

where $\mu_n = \langle \mathbf{e} \rangle_i$ is the mean value of the unit vector of the moment orientation in the chain.

Writing in the Fokker-Planck equation (6) φ instead of p and ε instead of u_1, and using the Kramers method and repeating the reasoning of Ref. [5], we get

$$\frac{dp_+}{dt} = -w_+p_+ + w_-p_-,$$

$$\frac{dp_-}{dt} = -w_-p_- + w_+p_+. \tag{30}$$

Here

$$w_+ = w_0 \exp(-\sigma + \alpha\cos\theta + \mu\gamma\beta_n),$$

$$w_- = w_0 \exp(-\sigma - \alpha\cos\theta - \mu\gamma\beta_n),$$

$$\beta_n = \frac{1}{n}\sum_{k,j,j\neq k} \frac{1}{|j-k|^3},$$

$$w_0 = \xi\frac{(2K)^{3/2}}{(2\pi T)^{1/2}}.$$

The summation in Eq. (29) is carried out over all particles in the chain. Strictly speaking, the energy of interaction of a given particle with the others depends on its place (number k) in the chain. Therefore, the parameter $\beta_{nk} = \Sigma_{j,j\neq k}|j-k|^{-3}$ must be used here instead of β_n. To simplify calculations we use the mean value β_n of β_{nk} over all particles.

In the framework of the approximation used the projection of the mean orientation vector of the n-particle chain on the chain axis is

$$\mu_n = p_+ - p_-. \tag{31}$$

Combining Eqs. (30) and (31), we arrive at the following nonlinear equation for μ_n:

$$\frac{d\mu_n}{dt} = -\frac{1}{\tau_0}[\mu_n\cosh(\alpha_H + \beta_n\gamma\mu_n) - \sinh(\alpha_H + \beta_n\gamma\mu_n)],$$

$$\tau_0 = \tau^o\frac{\exp(\sigma)}{\sigma^{1/2}}, \quad \tau^o = \frac{\pi^{1/2}}{\xi K}, \quad \alpha_H = \alpha\cos\theta. \tag{32}$$

When $\alpha=0$, the stationary solution of Eq. (32) satisfies the equation

$$\mu_0 = \tanh(\beta_n\gamma\mu_0). \tag{33}$$

If the product $\beta_n\gamma$ is large enough (only for this situation can one expect the occurrence of chains in a colloid), this equation has a nonzero solution. That is, this is the case of interest to us.

Let us write $x_n = \mu_n - \mu_0$. If $|x_n| \ll \mu_0$ and $\alpha \ll 1$, Eq. (32) can be rewritten as

$$\frac{dx_n}{dt} = -\frac{1}{\tau_{1n}}x_n + \alpha_H\frac{1}{\tau_0\cosh(\beta_n\gamma\mu_0)},$$

$$\tau_{1n} = \frac{\tau_0}{\cosh(\beta_n\gamma\mu_0)\{1+\gamma\beta_n[\mu_0\tanh(\beta_n\gamma\mu_0)-1]\}}. \tag{34}$$

The dynamical equations (32) and (34) describe response of the chain to a weak external field when μ_n is in the vicinity of the initial equilibrium value $\pm\mu_0$. This means that the period of the oscillating field must be much less than the characteristic time of reorientation of μ_n in the direction opposite to the initial direction of this vector. This time will be estimated below.

Let $\alpha = \alpha_0\exp(i\omega t)$. The projection x_{Hn} of x on the direction of this field is

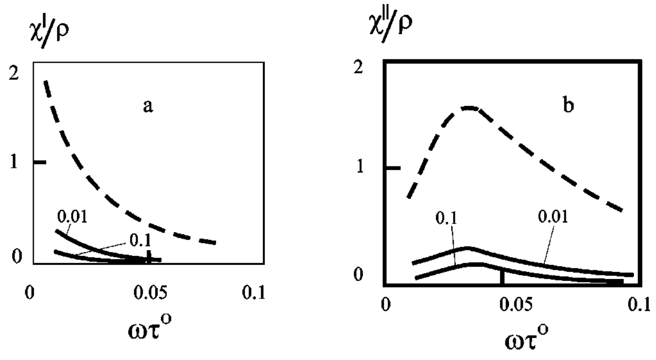

FIG. 4. Frequency dependences of real (a) and imaginary (b) parts of the high-frequency initial dynamical susceptibility of a ferrocolloid with chains (solid lines) and with single individual particles (dashed lines) when $\sigma=5$, $\gamma_0=3$, $\gamma=3$. Figures near curves are values of ρ.

$$x_{Hn}=x_n\cos^2\theta,\quad x_n=\kappa_n\alpha_0\cos^2\theta\exp(i\omega t),$$

$$\kappa_n=\kappa_n'-i\kappa_n'',\quad \kappa_n'=\frac{\tau_{1n}^o}{\tau_0\cosh(\beta_n\gamma\mu_0^o)}\,\frac{1}{1+(\omega\tau_{1n}^o)^2},$$

$$\kappa_n''=\omega\tau_{1n}^o\kappa_n'. \tag{35}$$

In order to determine the high-frequency complex susceptibility χ of the colloid, one needs to average relation (35) over all orientations and sizes of the chains.

For the sake of definiteness, let us suppose that this colloid was solidified in zero magnetic field. Therefore, the probabilities of all θ are identical. In view of this fact, we get for the macroscopic magnetization

$$M=\frac{m}{2}\sum_n x_n n g_n=\chi H. \tag{36}$$

Substituting x_n from Eq. (35) into Eq. (36), we arrive at the following expression for the effective complex high-frequency susceptibility:

$$\chi=\frac{3}{\pi}\gamma v\sum_n \kappa_n n g_n. \tag{37}$$

Using Eqs. (24) and (25), we find the distribution function g_n for the colloid frozen in zero field:

$$g_n=x_0^n\exp(-2\gamma_0),$$
$$x_0=\frac{1+2y_0-\sqrt{1+4y_0}}{2y_0},\quad y_0=\rho\exp(2\gamma_0). \tag{38}$$

Here and below γ_0 is the value of γ at the temperature of colloid solidification.

The frequency dependences of the real χ' and imaginary χ'' parts of χ are given in Figs. 4 and 5. These figures demonstrate that an increase of interparticle interaction leads to a decrease of susceptibility normalized to ρ provided that the signal frequency is small enough. It is a somewhat unusual result because, as a rule, the magnetodipole interaction increases the susceptibility of ferrocolloids (see, for example, Refs. [9–13] and Figs. 1 and 2). In order to explain this case let us rewrite Eq. (32) for small α as follows:

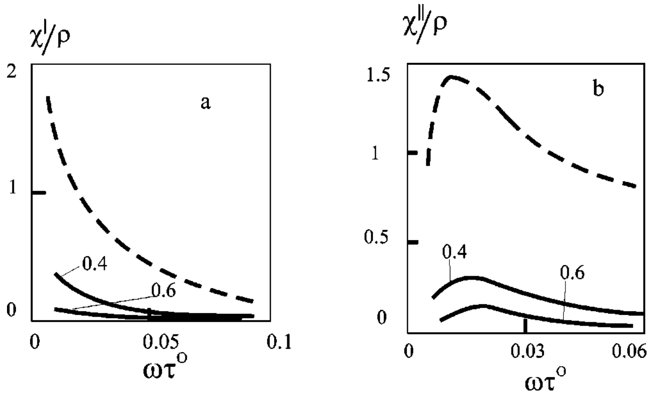

FIG. 5. The same as in Fig. 4 when $\rho=0.05$. Figures near curves correspond to $\gamma=\gamma_0$.

$$\frac{d\mu_n}{dt}=-\frac{1}{\tau_0}\frac{dU_n}{dt},$$
$$U_n=U_{n0}+\alpha_H u_n, \tag{39}$$
$$U_{n0}=\int[\mu_n\cosh(\beta_n\gamma\mu_n)-\sinh(\beta_n\gamma\mu_n)]d\mu_n,$$
$$u_n=\int[\mu_n\sinh(\beta_n\gamma\mu_n)-\cosh(\beta_n\gamma\mu_n)]d\mu_n.$$

Due to the strong inequality $\beta_n\gamma\gg1$ the effective potential U_{n0} as a function of μ_n has two deep pits and a high barrier between them. These pits correspond to solutions $\pm\mu_0$ of Eq. (33). When the product $\beta_n\gamma$ increases, the shape of the potential U_{n0} near $\pm\mu_0$ becomes sharper and the value $u_n(\mu_0)$ decreases. The relaxation of μ_n to $\pm\mu_0$, therefore, becomes faster (the time τ_{1n} decreases) and it is more difficult for the external field to make a deflection μ_n from its initial value. Therefore, the corresponding susceptibility decreases. It should be noted that a decrease of the initial susceptibility (normalized to ρ) of solid ferrocolloids was observed in the experiments of Ref. [8].

The temperature dependences of χ' are shown in Fig. 6. The temperature corresponding to the maximum of χ' is seen to increase with an increase of the interparticle interaction.

VI. LOW-FREQUENCY SUSCEPTIBILITY

In this section we will estimate the ferrocolloid complex susceptibility corresponding to the response to a magnetic field with a period that is less than or of the order of the characteristic time of crossing over the barrier of the effective potential U_{n0}. This time will be estimated.

As mentioned above, the dynamical equation (39) cannot describe this crossing, which can take place only due to the action of thermal fluctuations of μ_n. In order to take them into account we use the method of random forces.

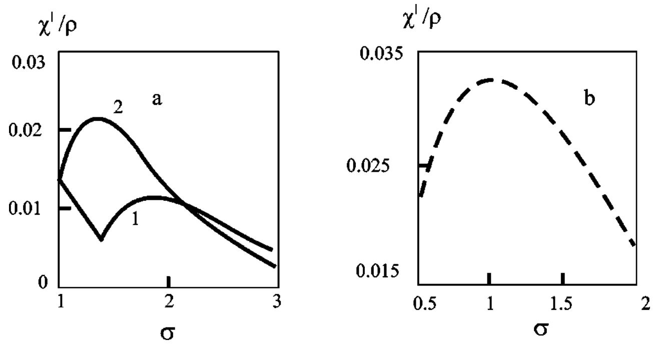

FIG. 6. Temperature dependences of real part of ''high-temperature'' initial susceptibility of a ferrocolloid with chains (a) and with single individual particles (b) at $\rho=0.1$, $\omega\tau^o=1.5$. Figures near curves (a) correspond to (1) $\gamma_1=\gamma/\sigma=0.6$, $\gamma_0=3$; (2) $\gamma_1=1$, $\gamma_0=5$. For curves (b) $\gamma_1=0.6$.

Let us rewrite Eq. (39) in the Langevin form,

$$\frac{d\mu_n}{dt}=-\frac{1}{\tau_0}\frac{dU_n}{\mu_n}+\zeta(t),$$

$$\langle\zeta(t)\rangle=0,\quad \langle\zeta(t)\zeta(t')\rangle=\sqrt{2B}\,\delta(t-t'),\tag{40}$$

$$B=\frac{T}{\tau_0}.$$

The following Fokker-Planck equation corresponds to this Langevin equation

$$\frac{\partial F_n}{\partial t}=\frac{\partial}{\partial\mu_n}\left(F_n\tau_0^{-1}\frac{dU_n}{d\mu_n}\right)+B\frac{\partial^2}{\partial\mu_n^2}F_n,\tag{41}$$

where $F_n(\mu_n)$ is the distribution function normalized to unity. Taking into account the presence of two deep pits in the plot of the function $U_n(\mu_n)$ and $\alpha\ll 1$, we arrive at

$$F_n=P_+\delta(\mu_n-\mu_0)+P_-\delta(\mu_n+\mu_0),$$

$$P_++P_-=1.\tag{42}$$

Using the Kramers method, we can easily obtain the following equation for $P_\pm$:

$$\frac{dP_+}{dt}=-W_+P_++W_-P_-,$$

$$\frac{dP_-}{dt}=-W_-P_-+W_+P_+,$$

$$W_\pm=W_0\exp\{\alpha_H[\pm u_n(\mu_0^o)-u_n(0)]-E_n\},\tag{43}$$

$$W_0=\frac{1}{2\pi\tau_0}\sqrt{\left.\frac{\partial^2U_{n0}}{\partial\mu_n^2}\right|_{\mu_n=\mu_0^o}\left(-\left.\frac{\partial^2U_{n0}}{\partial\mu_n^2}\right|_{\mu_n=0}\right)},$$

$$E_n=U_{n0}(0)-U_{n0}(\mu_0^o).$$

By definition, the mean moment of the particle in the chain is

$$M_n=\int\mu_nF_nd\mu_n=P_+-P_-.\tag{44}$$

Combining the first two relations of Eq. (43), we get the equation for M_n,

$$\frac{dM_n}{dt}=-M_n(W_++W_-)+W_--W_+$$

$$\approx -M_n2W_0\exp(-E_n)+\alpha_Hu_n^o2W_0\exp(-E_n),$$

$$u_n^o=u_n(\mu_0^o).\tag{45}$$

For a weak oscillating magnetic field $\alpha=\alpha_0\exp(i\omega t)$ ($\alpha_0\ll 1$), the projection of the moment M_n on the direction of the field is as follows:

$$M_{Hn}=X_n\alpha_0\cos^2\theta\exp(i\omega t),$$

$$X_n=X_n'-iX_n'',$$

$$X_n'=\frac{u_n^o}{1+(\omega\tau_{2n})^2},\quad X_n''=\frac{u_n^o\omega\tau_{2n}}{1+(\omega\tau_{2n})^2},\tag{46}$$

$$\tau_{2n}=\frac{\exp(E_n)}{2W_0},$$

$$u_n^o=u_n(\mu_0^o).$$

The parameter τ_{2n} is the characteristic time of opposite-sense remagnetization of the chain. Estimates show that for $n\geqslant 2$ this time depends on n very weakly. If the period of the external field is much more than τ_{2n}, it is a high-frequency signal for us. If the period is of the order of τ_{2n} or less, it is a low-frequency signal.

Using Eq. (46) just as we have done with Eq. (37), we arrive at the following expression for the effective complex low-frequency susceptibility:

$$X=X'-iX'',$$

$$X'=\frac{3}{\pi}\gamma\sum_n X_n'ng_nv,\quad X''=\frac{3}{\pi}\gamma\sum_n X_n''ng_nv\tag{47}$$

(we suppose again that the ferrocolloid was solidified in zero field).

The results of calculations of the frequency dependences of X are given in Figs. 7 and 8. Unlike the situation with the high-frequency susceptibility, the presence of chains increases the low-frequency susceptibility and decreases the frequency ω_c corresponding to the maximum of X''. Hence, two maxima instead of one can occur on the plot of frequency dependence of the imaginary part of the solid ferrocolloid susceptibility if heterogeneous chainlike aggregates occur in the system. The distance between these maxima increases with increasing magnetic interaction between the particles.

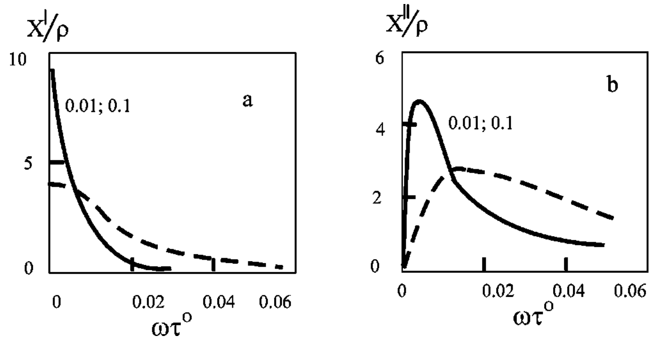

FIG. 7. Frequency dependences of real (a) and imaginary (b) parts of the low-frequency initial susceptibilities of a ferrocolloid with chains (solid lines) and with separate particles (dashed lines) when $\sigma=5$, $\gamma=\gamma_0=4$. Figures near curves are values of ρ.

Figure 9 shows the temperature dependences of X'. An increase of the interparticle interaction increases the temperature corresponding to the maximum of this function.

The plots of ω_c as a function of σ and ρ are given in Fig. 10. This frequency depends very strongly on temperature and, in contrast, weakly on the concentration ρ. It should be noted that in [7,8] the results of measurements of the dynamical susceptibility of solid ferrocolloids were described by the well-known empirical formula of Vogel-Fulcher for dipole-glass systems

$$\omega_c \sim \exp\left(-\frac{E_a}{T-T_0}\right),$$

where E_a is the Néel activation energy of the single particle, T_0 is the temperature of the dipole-glass phase transition (this temperature was estimated in [7,8] as $T_0 \sim \rho^s$, where $s=0.8$ [7] and $s=0.4$ [8]). For this reason the results of [7,8] were interpreted as evidence of existence of a glasslike state in colloids. The plots of Fig. 10 correspond to these forms of the Vogel-Fulcher law if $T \gg T_0$. We would like to note that the measurements of [7,8] were performed when the inequality $T > T_0$ holds. Therefore, our estimates allow us to suppose that the glasslike response of solid ferrocolloids to an external field can be explained as the effect of the presence of heterogeneous aggregates in these systems.

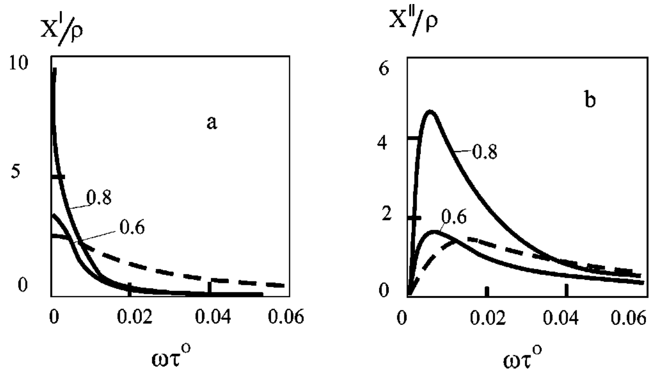

FIG. 8. The same as for Fig. 7 for $\rho=0.05$. Figures near curves are values of $\gamma=\gamma_0$.

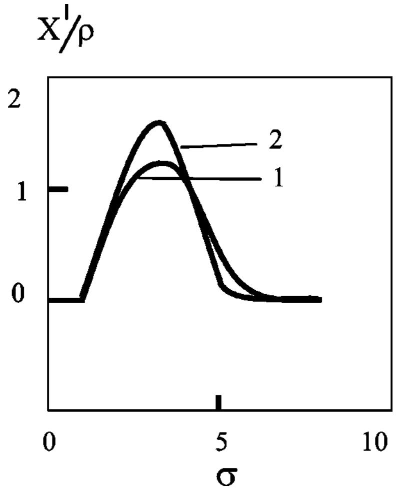

FIG. 9. Temperature dependences of the real part of the initial susceptibility of a ferrocolloid with chains when $\omega\tau^o=0.02$, $\rho=0.1$. Figures near curves correspond to (1) $\gamma_1=0.7$, $\gamma_0=3.5$; (2) $\gamma_1=0.8$, $\gamma_0=4$.

VII. CONCLUSION

A theoretical analysis of the dynamical susceptibility of a ferrocolloid taking account of the dipole-dipole interaction is presented. Two kinds of system are studied. The first is a moderately concentrated homogeneous ferrocolloid; the second is a ferrocolloid with heterogeneous chainlike aggregates. For a system of the first kind interparticle interaction increases both the real and imaginary parts of the dynamical susceptibility and decreases the frequency of the signal corresponding to the maximum of the imaginary part of the susceptibility. In experiments it should be evident as an increase in the characteristic magnetization relaxation time of the system.

For systems with chainlike aggregates the characteristic time τ_c of inverse remagnetization of the chain is of fundamental importance. If the period of the signal is much less than τ_c (high-frequency signal), then the components of the corresponding complex susceptibility decrease with increasing magnetodipole interaction of the particles. The frequency corresponding to the maximum of the imaginary part of the complex susceptibility in this case increases (i.e., the characteristic relaxation time decreases). If the period of the signal is of the order of τ_c or larger, then an increase of interparticle

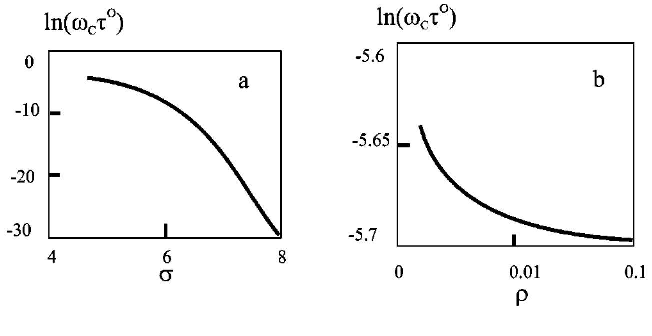

FIG. 10. Temperature (a) and concentration (b) dependences of ω_c at $\gamma_1=0.8$, $\gamma_0=4$.

interaction leads to an increase in the components of the susceptibility and to a decrease of the frequency ω_c corresponding to the maximum of its imaginary part. Therefore, the presence of heterogeneous aggregates in a solid ferrocolloid should lead to the occurrence of two maxima (instead of one) in the frequency dependence of the imaginary part of the susceptibility. A strengthening of the interparticle interaction leads to an increase in the distance between these maxima.

The frequency ω_c of the maximum of the imaginary part of the low-frequency susceptibility of a colloid with chains decreases very quickly (much more rapidly than for the colloid with separate particles) as the temperature decreases. With increasing concentration of particles ω_c also decreases, but more slowly. In a qualitative sense, our results are consistent with the variants of the empirical Vogel-Fulcher law for dipole glasses that were used in [7,8]. This allows us to make the proposal that the glasslike behavior of the dynamical susceptibility of solid ferrocolloids detected in a body of experiments may be explained by the presence of heterogeneous aggregates.

Finally, we would like to note that our results are in qualitative agreement with experiments [1–3,6–8]. At the same time, a quantitative agreement can hardly be expected, because commercial ferrofluids, used in experiments, are polydisperse. The polydispersity of ferrocolloids affects their macroscopic dynamical properties very strongly. However, to understand the main physical consequences of the interparticle interactions for the properties of these systems, one needs, first, to analyze monodisperse models. That is the aim of this work.

ACKNOWLEDGMENT

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