Dynamic magnetic susceptibility of a ferrofluid: The influence of interparticle interactions and ac field amplitude

Michael S. Rusanov, Vladimir S. Zverev, and Ekaterina A. Elfimova*
Department of Theoretical and Mathematical Physics, Institute of Natural Sciences and Mathematics, Ural Federal University, 51 Lenin Avenue, Ekaterinburg 620000, Russia

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Based on numerical results of dynamic susceptibility, a simple theory of the dynamic response of a ferrofluid to an ac magnetic field is obtained that includes both the effects of interparticle dipole-dipole interactions and the dependence on field amplitude. Interparticle interactions are incorporated in the theory using the so-called modified mean-field approach. The new theory has the following important characteristics: in the noninteracting regime at a weak ac field, it gives the correct single-particle Debye theory results; it expands the applicability of known theories valid for high concentrations [Ivanov, Zverev, and Kantorovich, Soft Matter **12**, 3507 (2016)] or large values of ac field amplitudes [Yoshida and Enpuku, Jpn. J. Appl. Phys. **48**, 127002 (2009)], in accordance with their applicability. The susceptibility spectra are analyzed in detail. It is demonstrated that interparticle dipole-dipole interactions and an increase in field amplitude have an opposite effect on the dynamic response of ferrofluids, so that at certain field amplitudes, relaxation processes in the system of interacting particles are determined by the characteristic relaxation times for an ideal paramagnetic gas. The new theory correctly predicts the dynamic susceptibility and characteristic relaxation times of a ferrofluid at high ac field amplitudes as long as the Langevin susceptibility $\chi_L \lesssim 1$, which is a complex characteristic of ferrofluid density and the intensity of interparticle dipole-dipole interactions.

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I. INTRODUCTION

Ferrofluids are stable colloidal suspensions of one-domain particles of ferromagnetic materials in carrier liquids [1]. Typical ferrofluids contain particles roughly 10 nm in diameter, meaning that the magnetic dipole moment reorients mainly due to Brownian rotational motion of the particle as a whole. Smaller nanoparticles exhibit superparamagnetism, in which the magnetic dipole moment flips through the Néel mechanism [1,2]. The frequency-dependent magnetic susceptibility $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$ is an important property of ferrofluids [3,4] that forms the basis of many applications [5–8]. For instance, the heating of a magnetic fluid with an ac magnetic field is proportional to the imaginary (out-of-phase) part $\chi''(\omega)$ [9]. This has led to applications in medicine such as localized heating (hyperthermia) and the destruction of diseased tissue [10–15].

The dynamic magnetic susceptibility of ferrofluids has been studied extensively, both experimentally and theoretically, and the literature is vast. From the theoretical point of view, the dynamic susceptibility can be predicted for diluted ferrofluids in a weak ac magnetic field by the Debye theory of polar media [16]. An increase in the ac field amplitude leads to significant changes in the dynamic susceptibility spectrum [17–22], which can be theoretically described quite reliably by the simple analytical expression proposed in [23]. Many attempts have been made to include the effects of dipole-dipole interactions on dynamic susceptibility [24–29]. In a recent work, an approach based on the so-called modified mean-field theory [30] was developed to enable interactions to be included in a systematic way, based on classical statistical mechanics [31]. The resulting expressions in [31] for a dynamic response of a ferrofluid to a weak ac magnetic field have a closed analytical form and represent first-order density corrections to the Debye susceptibility.

Among the great variety of theories, the main advantages of the aforementioned three theories [16,23,31] are simple analytical expressions that are easy to use for the computation and prediction of the dynamic susceptibility of a ferrofluid. It is worth noting that each of these theories has its own range of applicability shown schematically in Fig. 1. The basic elements of these theories [16,23,31] are outlined below.

A. The Debye theory

In the absence of dipole-dipole interactions and in the presence of a weak ac magnetic field $\mathbf{H}(t) = he^{i\omega t}\hat{\mathbf{h}}$ (h is the amplitude, ω stands for the angular frequency, $\hat{\mathbf{h}}$ is the unit vector in the direction of the field, and t denotes time), the mathematical problem of computing the susceptibility spectrum is rather straightforward [16,32]. The result is known as the Debye theory:

$$\chi_D(\omega) = \frac{\chi_L}{1 - i\omega\tau_B} = \chi_D{}'(\omega) + i\chi_D{}''(\omega),$$
$$\chi_D{}'(\omega) = \frac{\chi_L}{1 + (\omega\tau_B)^2},$$
$$\chi_D{}''(\omega) = \frac{\chi_L\omega\tau_B}{1 + (\omega\tau_B)^2}. \quad (1)$$

*Ekaterina.Elfimova@urfu.ru

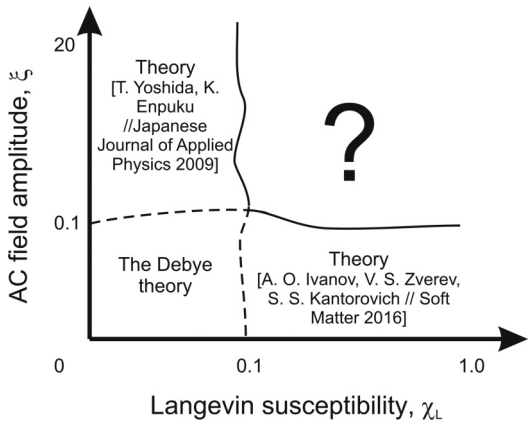

FIG. 1. Diagram of theoretical knowledge on dynamic susceptibility. The theories presented in the diagram give simple analytical expressions for the real and imaginary parts of susceptibility in terms of field amplitude and the Langevin susceptibility.

It is assumed that ferroparticles undergo Brownian relaxation only with the Brownian rotation time τ_B. The zero-frequency limit of the Debye theory gives the Langevin static susceptibility $\chi_L = \mu_0 m^2 \rho / 3 k_B T$, which is proportional to the numerical ferroparticle concentration ρ and the square of the particle magnetic moment m; μ_0 is the vacuum magnetic permeability, and $k_B T$ stands for the thermal energy. The analytical expressions for real and imaginary susceptibility (1) are quantitatively accurate for diluted ferrofluids as long as $\chi_L \lesssim 0.1$ and $\xi \ll 1$, where $\xi = \mu_0 m h / k_B T$ is a ratio of the interaction energy between the particle magnetic moment and the ac magnetic field to the thermal energy $k_B T$. The dimensionless parameter ξ characterizes the amplitude of the ac magnetic field.

B. Theory of the dynamic response of noninteracting magnetic particles to an ac field of arbitrary amplitude

Approximate equations that describe the dynamic susceptibility of ferrofluids at a high ac field amplitude $\xi \gg 1$ were obtained in [23]. This theory is a modification of the Debye equations:

$$\begin{aligned} \chi_Y(\omega) &= \chi_Y{}'(\omega) + i\chi_Y{}''(\omega), \\ \chi_Y{}'(\omega) &= \frac{\chi(0)}{1+(\omega\tau_e)^2}, \\ \chi_Y{}''(\omega) &= k\frac{\chi(0)\omega\tau_e}{1+(\omega\tau_e)^2}, \end{aligned} \tag{2}$$

where $\chi(0)$, k, and τ_e are functions of the ac field amplitude ξ,

$$\frac{\chi(0)}{\chi_L} = 1 - \frac{0.0636\xi^2}{1+0.18\xi+0.0659\xi^2}, \tag{3}$$

$$\tau_e = \frac{\tau_B}{\sqrt{1+0.07\xi^2}}, \tag{4}$$

$$k = 1 + \frac{0.024\xi^2}{1+0.18\xi+0.033\xi^2}. \tag{5}$$

Formulas (2)–(5) are obtained by approximating the numerical solution of the Fokker-Planck equation for the probability density of the magnetic moment orientation [23]. To solve the Fokker-Planck equation, the probability density was represented as a series in terms of the Legendre polynomials with unknown time-dependent coefficients. Substitution of this series into the Fokker-Planck equation made it possible to obtain recurrent relations linking three consecutive coefficients of the series. The truncation at some arbitrary order in recurrent relations gives a closed set of differential equations, which was solved numerically. The truncation order was determined from the condition of the convergence of the solution and depended on the amplitude of the alternating field.

Like the Debye theory, dynamic susceptibility (2)–(5) does not take into account interparticle dipole-dipole interactions, and it can be applied only to dilute ferrofluids with $\chi_L \lesssim 0.1$. It was shown in [23] that the analytical expressions (2)–(5) are quantitatively correct for an ac field amplitude of at least $\xi \lesssim 20$.

C. First-order modified mean-field theory

Interparticle dipole-dipole interactions lead to significant changes in the dynamic susceptibility spectrum [28,29,33,34]. Recently, a new dynamic theory of interacting dipolar particles in the Brownian-relaxation regime was proposed [31]:

$$\begin{aligned} \chi_I(\omega) &= \chi_I{}'(\omega) + i\chi_I{}''(\omega), \\ \chi_I{}'(\omega) &= \chi_D{}'(\omega) + \tfrac{1}{3}([\chi_D{}'(\omega)]^2 - [\chi_D{}''(\omega)]^2), \\ \chi_I{}''(\omega) &= \chi_D{}''(\omega)\big(1 + \tfrac{2}{3}\chi_D{}'(\omega)\big). \end{aligned} \tag{6}$$

The theory is based on the so-called modified mean-field approach. In a low-concentration, noninteracting regime, it gives the correct Debye theory results. At the zero-frequency limit, it yields static susceptibility corresponding to the first-order modified mean-field theory $\chi = \chi_L(1 + \chi_L/3)$. The theory was tested on the results of Brownian-dynamics simulations [35] and experimental data [36]. It was demonstrated that the theory (6) correctly predicts the dynamic susceptibility of ferrofluids as long as $\chi_L \lesssim 1$ and the ac field amplitude is $\xi \ll 1$.

Thus, the known experimental and theoretical results of the dynamic response of a ferrofluid to the ac magnetic field demonstrate the strong dependence of the susceptibility spectrum on the amplitude of the ac field and on interparticle dipole-dipole interactions. The problem is that the region of high ac field amplitudes and the Langevin susceptibility, indicated in Fig. 1 by a question mark, is still an unexplored area. There are no simple analytical expressions to predict dynamic susceptibility in this range of parameters, which is most interesting for the application of ferrofluids. The aim of the current work is to fill this gap by describing the effects of both interparticle dipole-dipole interactions and field amplitude on dynamic susceptibility and relaxation processes in ferrofluids.

II. MODEL AND NUMERICAL ALGORITHM

A. Model and basic properties

The ferrofluid is modeled as an ensemble of N spherical single-domain magnetic particles with equal diameters

d, dispersed in a liquid. The direction of the ith magnetic moment is the vector $\mathbf{m}_i = m\hat{\mathbf{m}}_i = m(\sin\theta_i\cos\varphi_i, \sin\theta_i\sin\varphi_i, \cos\theta_i)$. The position of the ith particle center is defined by coordinates of the radius-vector $\mathbf{r}_i = r_i\hat{\mathbf{r}}_i = r_i(\sin\zeta_i\cos\psi_i, \sin\zeta_i\sin\psi_i, \cos\zeta_i)$. To avoid demagnetization corrections, we chose a sample container shaped like a highly elongated cylinder with radius R and volume V aligned along the laboratory Oz axis; the applied ac magnetic field $\mathbf{H} = h\cos(\omega t)\hat{\mathbf{H}}$ is in the same direction, $\hat{\mathbf{H}} = (0, 0, 1)$. The internal macroscopic field inside the sample is equal to the external magnetic field $\mathbf{H}$, and the interaction energy $U_H(i)$ between the ith particle magnetic moment and the magnetic field can be written in the Zeeman form

$$U_H(i) = -\mu_0(\mathbf{m}_i \cdot \mathbf{H}) = -\mu_0 mH\cos(\omega t)\cos\theta_i. \quad (7)$$

The interparticle dipole-dipole interaction is

$$U_d(i, j) = -\frac{\mu_0 m^2}{4\pi r_{ij}^3}[3(\hat{\mathbf{m}}_i \cdot \hat{\mathbf{r}}_{ij})(\hat{\mathbf{m}}_j \cdot \hat{\mathbf{r}}_{ij}) - (\hat{\mathbf{m}}_i \cdot \hat{\mathbf{m}}_j)], \quad (8)$$

which depends on the distance between the centers of two ferroparticles $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i = r_{ij}\hat{\mathbf{r}}_{ij}$ and the mutual orientation of their magnetic moments.

Since the Néel relaxation time in the dynamics of single-domain particles in a liquid is much longer than the Brownian relaxation time, we assume that particles undergo Brownian relaxation only. Due to the symmetry of the system, the orientation of each magnetic moment need only be described with the polar angle θ_i. The rotational motion of the magnetic moment of the randomly chosen particle (with number 1, for example) is described by the probability density $W = W(t, x)$, $x = \cos\theta_1$, which is a solution of the Fokker-Planck equation:

$$2\tau_B\frac{\partial W}{\partial t} = \frac{\partial}{\partial x}\left[(1 - x^2)\left(\frac{\partial W}{\partial x} + W\frac{\partial U}{\partial x}\right)\right], \quad (9)$$

where U is the potential energy of a dipole in units of the thermal energy k_BT. $W(t, x)$ satisfies the normalization condition:

$$\int_{-1}^{1} W(t, x)dx = 1. \quad (10)$$

In the absence of interparticle interactions [as denoted by the ideal case (id)], the potential energy of a randomly chosen dipole (with number 1) in units of k_BT is simply

$$U = U_{\rm id}(1) = \frac{U_H(1)}{k_BT} = -\xi x\cos(\omega t). \quad (11)$$

To take into account dipole-dipole interactions, we follow the earlier work of Ref. [31], where single-particle energy $U_{\rm id}(1)$ was extended by incorporating dipole-dipole interactions on the basis of the first-order modified mean-field model [30,31]:

$$U = U_{\rm int}(1) = \frac{1}{k_BT}(U_H(1) + \rho\langle U_d(1, 2)W^{\rm id}(2)\Theta(1, 2)\rangle_2), \quad (12)$$

where $W^{\rm id}(2) = W^{\rm id}(t, x_2)$ is the orientational probability for the magnetic moment of particle 2 in an ideal (noninteracting) system. The Heaviside step-function $\Theta(1, 2)$ describes the impenetrability of two dipolar particles. The angular brackets denote averaging over all possible orientations and positions of particle 2:

$$\langle U_d(1, 2)W^{\rm id}(2)\Theta(1, 2)\rangle_2 = \int d\hat{\mathbf{m}}_2\int d\hat{\mathbf{r}}_2 U_d(1, 2)W^{\rm id}(2). \quad (13)$$

$$\int d\hat{\mathbf{m}}_2 = \frac{1}{4\pi}\int_{-1}^{1} dx_2\int_0^{2\pi} d\varphi_2, \quad \int d\hat{\mathbf{m}}_2 \cdot 1 = 1,$$

$$\int d\hat{\mathbf{r}}_2 = \lim_{R\to\infty}\int_0^{2\pi} d\psi_2\int_0^{\pi}\sin\zeta_2 d\zeta_2\int_d^{R/\sin\zeta_2} r_2^2 dr_2,$$

$$\int d\hat{\mathbf{r}}_2 \cdot 1 = V.$$

Here the integral over $d\hat{\mathbf{r}}_2$ corresponds to the averaging over all possible positions of the 2th particle inside the sample volume V taking into account its cylindrical shape, and R has a meaning of the cylinder radius, which is infinitely larger than the particle diameter d in the thermodynamic limit. The cylindrical shape of the container allows us to avoid demagnetization corrections, which is important only in the case of interacting particles. To take into account the excluded volume occupied by the first particle, we use the particle diameter d in the lower limit of integration with respect to the variable dr_2 (r_2 is the distance between centers of particles 1 and 2). Substitution of the result of the integration (13) into Eq. (12) gives

$$U = U_{\rm int}(1) = -\left[\xi\cos(\omega t) + \frac{\chi_L}{2}\int_{-1}^{1} W^{\rm id}(t, x_2)x_2 dx_2\right]x. \quad (14)$$

This potential is first order in χ_L, which is a complex characteristic of ferrofluid density and the intensity of interparticle dipole-dipole interactions. It should be noted that the model (9), (10), and (14) corresponds to a monodisperse ferrofluid. The direct application of this model to experimental results is complicated by the polydispersity of real ferrofluids. Nevertheless, the extension of this model to the polydisperse case is possible, and it was done in [36] for the case of small amplitudes of the ac field. Additionally, it was shown in [36] that the results of the polydisperse theory are in good agreement with experimental data in a wide temperature range. In this work, we restrict our consideration of the monodisperse case, where the effects of interactions are more pronounced than in a polydisperse ferrofluid. It is worth noting that in Ref. [35] the monodisperse model (9), (10), and (14) showed a good agreement with the data of the Brownian dynamic computer simulation for the case of small amplitudes of the ac field.

The magnetization M is determined by the one-particle probability density $W(t, x)$:

$$M(t) = \rho m\int d\hat{\mathbf{m}}_1(\hat{\mathbf{m}}_1 \cdot \hat{\mathbf{H}})W(t, x) = \frac{\rho m}{2}\int_{-1}^{1} xW(t, x)dx. \quad (15)$$

The real $\chi'(\omega)$ and imaginary $\chi''(\omega)$ parts of dynamic susceptibility are defined as the first term in the Fourier series

of $M(t)$:

$$\chi'(\omega) = \frac{\omega}{\pi h}\int_0^{\frac{2\pi}{\omega}} M(t)\cos(\omega t)dt,$$
$$\chi''(\omega) = \frac{\omega}{\pi h}\int_0^{\frac{2\pi}{\omega}} M(t)\sin(\omega t)dt. \quad (16)$$

B. Numerical method

The Fokker-Planck equation can be solved exactly in some cases. Usually, the numerical solution of the Fokker-Planck equation is based on the expansion of the unknown function W through a series in terms of eigenfunctions and the numerical calculation of the finite number of terms in this series. The number of terms that must be taken account for the correct result depends on the parameters of the system and cannot be determined in advance. This means that the error of approximation can be underestimated. In the current work, the finite-difference scheme is used for the direct numerical solution of Eq. (9). This scheme was first proposed in [37] for solving convection-diffusion problems. In [37], the criteria of convergence of the numerical approximation to the solution were also proved. Since the first term on the right-hand side of Eq. (9) can be considered as a diffusion term and the second is a convection term, the numerical algorithm [37] can easily be carried over to the solution of Eq. (9). The advantage of this method is numerical stability even when the convection term predominates in the Fokker-Planck equation. The numerical algorithm proposed in [37] has already been successfully applied by some of the current authors to solve the Fokker-Planck equation to describe the behavior of immobilized single-domain magnetic particles [38]. The basic elements of this algorithm are outlined here.

The two-dimensional space (t, x) was split into a uniform grid $\{(t_k, x_i)|\ t_k = t_{k-1} + h_t,\ x_k = x_{k-1} + h_x,\ t_0 = 0, x_0 = -1 + h_x/2\}$ with a finite number of nodes. h_t, h_x determine the grid cell size in t and x directions. Indexes k and i vary from 0 to their final values $N_t = T_f/h_t, N_x = 2/h_x - 1$ correspondingly, where T_f is the final moment of time in the calculation. Let us also use the notation $W_{k,i} = W(t_k, x_i)$. The discrete form of Eq. (9) is

$$\frac{\exp(-\delta\, h_t)\, W_{k,i} - W_{k-1,i}}{h_t} + (C_2 + D + \delta)[\exp(-\delta\, h_t)\, W_{k,i}] = 0,\ i = 0, \ldots, N_x. \quad (17)$$

D and C_2 are discrete operators for diffusion and convection terms correspondingly:

$$DW_{k,i} = \frac{1}{h_x^2}\left[- f\left(x_i + \frac{h_x}{2}\right)(W_{k,i+1} - W_{k,i}) + f\left(x_i - \frac{h_x}{2}\right)(W_{k,i} - W_{k,i-1})\right],$$
$$f(x) = (1 - x^2),$$
$$C_2 W_{k,i} = \frac{1}{2h_x}\left[v\left(t^*, x + \frac{h_x}{2}\right)(W_{k,i+1} + W_{k,i})\right] - \frac{1}{2h_x}\left[v\left(t^*, x - \frac{h_x}{2}\right)(W_{k,i} + W_{k,i-1})\right],$$
$$t^* = \frac{t_{k+1} + t_k}{2}, \quad v(x) = \frac{\partial U}{\partial x}(1 - x^2).$$

In Eq. (17), δ can be considered as a regularization parameter used to make the numerical scheme unconditionally stable: it is equal to $\frac{1}{2}\max|v_x'|$. In our calculations, $\delta = \xi$ was used for both interacting and noninteracting cases.

At every $t = t_k$, Eq. (17) is a set of linear algebraic equations in unknown variables $W_{k,0}, W_{k,1}, \ldots, W_{k,N_x}$ which are found through the tridiagonal matrix algorithm. To satisfy condition (10), normalization is carried out:

$$W_{k,i}^{\text{norm}} = \frac{W_{k,i}}{h_x \sum_{i=0}^{N_x} W_{k,i}},$$

therefore

$$h_x \sum_{i=0}^{N_x} W_{k,i}^{\text{norm}} = 1.$$

The magnetization and dynamic susceptibility are determined by formulas (15) and (16), where the integrals of the discrete function $W_{k,i}^{\text{norm}}$ are calculated via the trapezium method.

C. Numerical algorithm testing

To validate the numerical algorithm and methodology, calculations were first run for the noninteraction system with potential energy (11). The numerical calculation was carried out on a grid with size $h_t = 0.001$ and $h_x = 0.01$. The susceptibility spectra of four simulated systems at a dimensionless ac field amplitude of $\xi = 0.01$, 1, 5, and 10 are shown in Fig. 2, as well as in theories (2)–(5). The Debye theory results from Eq. (1) are also represented for the weak ac field $\xi = 0.01$. The agreement between the numerical results and theories is excellent.

Figure 3 shows the dynamic susceptibility for systems with interactions in the weak ac field $\xi = 0.01$ at Langevin susceptibilities of $\chi_L = 0.1$, 0.5, 1, and 2. The numerical results are compared with predictions from the first-order modified mean-field theory [Eq. (6)] and for the diluted system $\chi_L = 0.1$ with the Debye theory [Eq. (1)]. The numerical solution is accurate over the full range of the Langevin susceptibility $\chi_L \leqslant 2$ at a low amplitude of the ac field.

These results show that the numerical algorithm and size grid are all sufficient for obtaining reliable results. It is also worth noting here that an increase in the field amplitude ξ and an increase in the Langevin susceptibility χ_L affect the susceptibility spectrum in different ways: an increase in the field amplitude leads to a decrease in the susceptibility and a shift to the right of the maximum of the imaginary part (Fig. 2); an increase in the Langevin susceptibility causes the reverse reaction—the susceptibility increases, and the maximum of the imaginary part shifts to the left (Fig. 3). These two effects compete with each other when high field amplitudes and

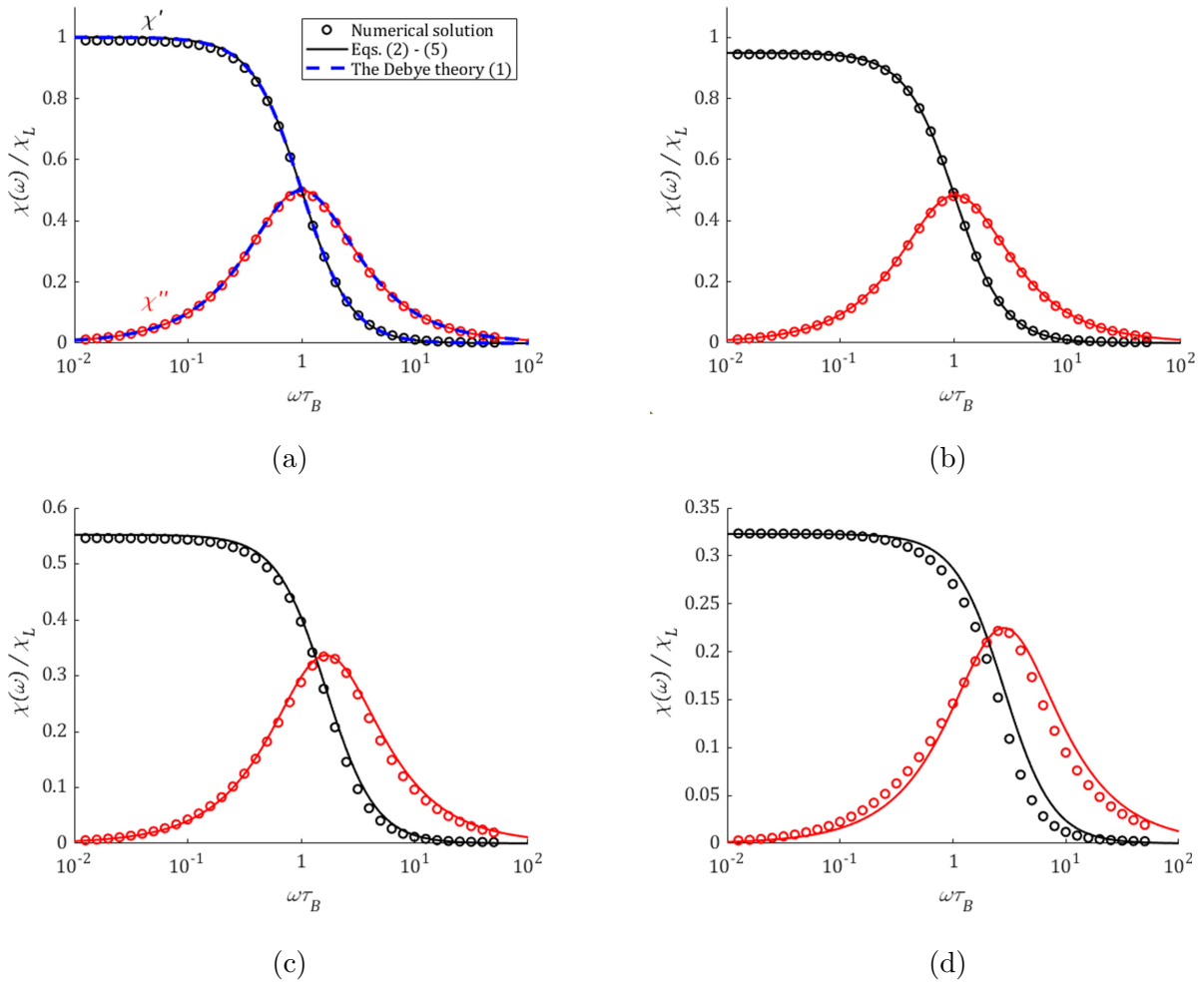

FIG. 2. The susceptibility spectra $\chi(\omega)/\chi_L$ of noninteracting particles at (a) $\xi = 0.01$, (b) $\xi = 1$, (c) $\xi = 5$, and (d) $\xi = 10$. The points are from numerical calculations; solid lines are from the Yoshida and Enpuku theory [23] [Eqs. (2)–(5) in this paper]. The Debye theory (1) is shown by the dashed line only in the range of its applicability for the weak ac field $\xi = 0.01$.

interparticle interactions are taken into account simultaneously. This will be demonstrated in Sec. III.

D. New theory

To obtain a simple analytical expression for the dynamic susceptibility of interacting particles in the ac field at an arbitrary amplitude, the method proposed by Yoshida and Enpuku [23] is used. Dynamic susceptibility is presented in form (2), where $\chi(0)$ is the value of the real part of the susceptibility at low frequencies, $1/\tau_e$ is the position, and $[k\chi(0)/2]$ is the maximum value of the imaginary part of the susceptibility. In general, $\chi(0)$, τ_e, and k are functions of ξ and χ_L. Forming analytical expressions for $\chi(0)$, τ_e, and k, the dependence on the Langevin susceptibility was taken into account up to χ_L^2 using the approximations proposed in [31]. The analytical dependence on ξ was similar to [23], but the coefficients before ξ were unknown. To determine them, the least-squares method was used: the numerical values $\chi(0)$, τ_e, and k for a system with $\chi_L = 0.4$ were approximated via analytical expressions with unknown coefficients. As a result, the following analytical expressions for dynamic susceptibility were obtained. These formulas take into account interparticle interactions and a dependence on the field amplitude:

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega),$$

$$\chi'(\omega) = \frac{\chi(0)}{1+(\omega\tau_e)^2}, \tag{18}$$

$$\chi''(\omega) = k\frac{\chi(0)\omega\tau_e}{1+(\omega\tau_e)^2},$$

$$\chi(0) = \chi_L\left(1+\frac{\chi_L}{3}\right)\left(1-\frac{0.101\xi^2}{1+0.276\xi+0.104\xi^2}\right), \tag{19}$$

$$\frac{1}{\tau_e} = \frac{1}{\tau_B}\sqrt{\left(1-\frac{\chi_L}{3}\right)^2+0.076\xi^2}, \tag{20}$$

$$k = 1+\frac{0.027\xi^2}{1+0.102\xi+0.047\xi^2}. \tag{21}$$

It is worth emphasizing that the new theory (18)–(21) was determined on the basis of numerical results for a system with the Langevin susceptibility $\chi_L = 0.4$. In what follows, it will be shown that expressions (18)–(21) are valid for systems with other values of χ_L.

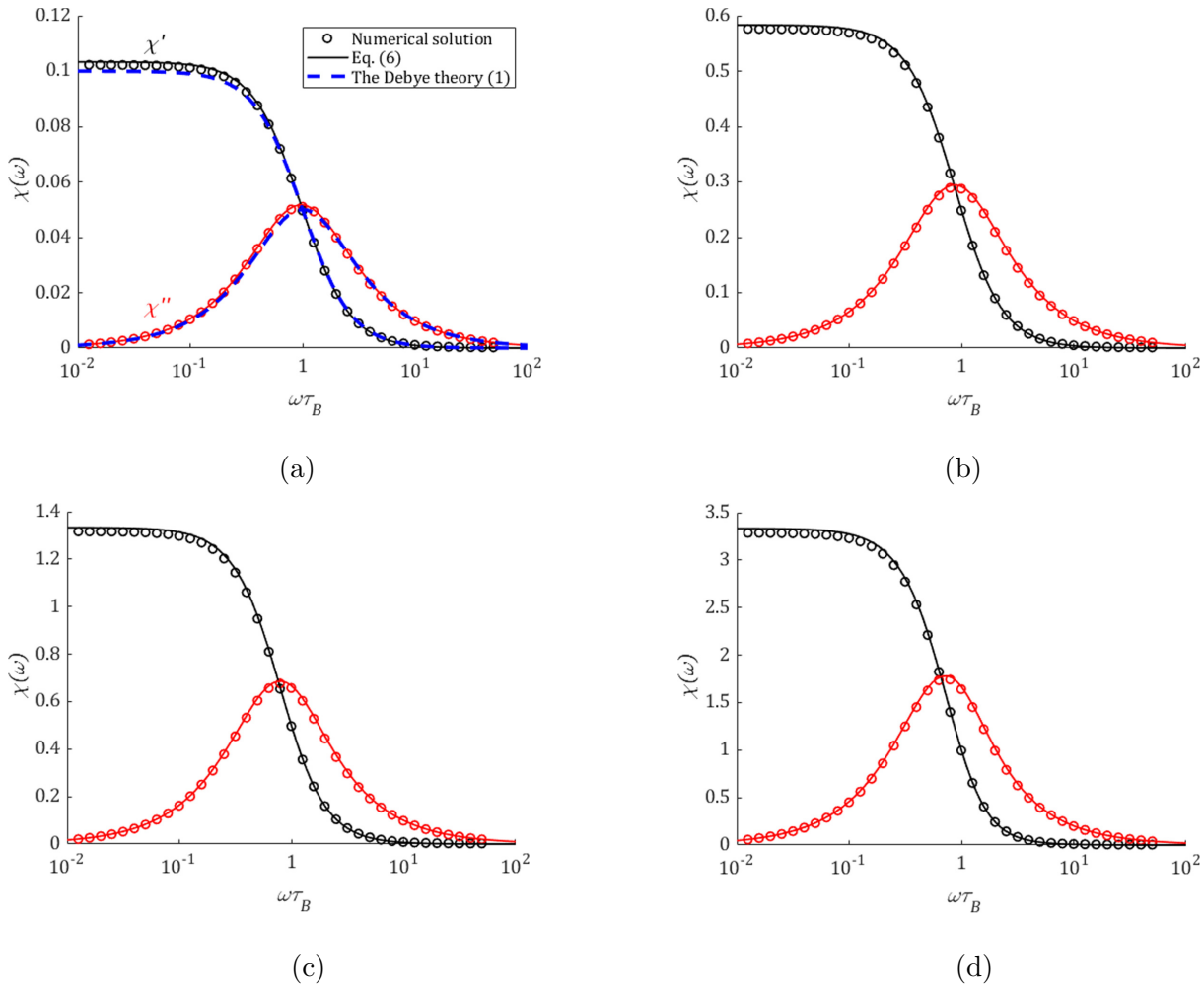

FIG. 3. The susceptibility spectra $\chi(\omega)$ of interacting particles in the weak ac field $\xi = 0.01$ with (a) $\chi_L = 0.1$, (b) $\chi_L = 0.5$, (c) $\chi_L = 1$, and (d) $\chi_L = 2$. The points are from numerical calculations, while the solid lines are from the Ivanov *et al.* theory [31] [Eq. (6) in this paper]. The Debye theory is shown by the dashed line only in the range of its applicability for the diluted system with $\chi_L = 0.1$.

III. RESULTS AND DISCUSSION

Figure 4 shows a comparison of dynamic susceptibility from numerical calculations and the results of the new theory (18)-(21) for particles with interactions. There are three systems with Langevin susceptibilities $\chi_L = 0.2$, 0.5, and 1 at amplitudes of the ac field $0.1 \leqslant \xi \leqslant 20$. For $\chi_L = 0.2$ and 0.5, the agreement between numerical and theoretical results is excellent at all values of ξ. For $\chi_L = 1$, small deviations are observed. In general, we can conclude that the new theory predicts dynamic susceptibility rather well over the range of parameters $\chi_L \lesssim 1$ and $\xi \lesssim 20$. As we noted before, interparticle interactions are taken into account in the Fokker-Planck equation in the framework of the first-order modified mean-field theory, i.e., the potential energy of a dipole (14) has the first order in terms of the Langevin susceptibility χ_L. This means that only pair interparticle interactions are included in the model. Three-particle and four-particle (and more) interactions become important in systems with high values of χ_L. In [35], it was demonstrated that the first-order mean-field approximation correctly predicts the dynamic susceptibility of ferrofluids as long as $\chi_L \lesssim 1$. Since the new theory is formed on the basis of the numerical solution of the Fokker-Plank equation with potential energy (14), the achieved region of validity for the new theory $\chi_L \lesssim 1$ is the utmost possible at this level of approximation. It is seen in Fig. 4 that for each value of χ_L, increasing the field amplitude leads to a decrease in susceptibility and a shift to the right of the maximum of the imaginary part $\chi''(\omega)$. The latter reflects a decrease in the characteristic relaxation time. So, increasing the field amplitude promotes a speed-up of the orientation relaxation of particles in the system.

The role of interparticle interactions in the dynamic susceptibility of ferrofluids is presented in Fig. 5 for a system with $\chi_L = 0.5$. The solid lines are from the new theory that takes into account interparticle interactions; the points are from Eqs. (2)–(5) for a noninteracting system. For each value of the ac field amplitude ξ, interparticle interactions increase dynamic susceptibility, reflecting stronger orientational correlations between particles and the growth of collective orientational dynamics. Besides, the lower the amplitude of the field, the greater the difference between the susceptibility

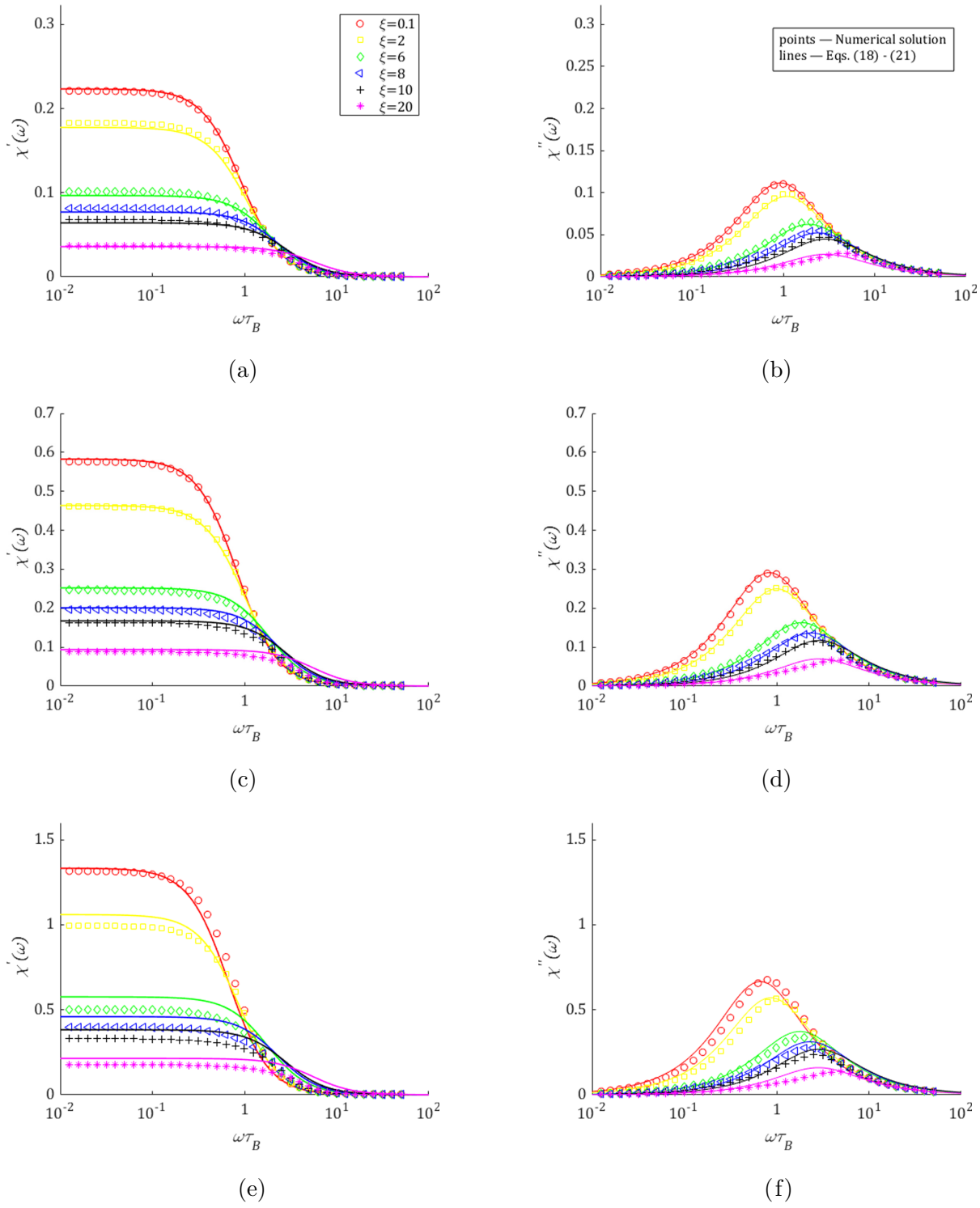

FIG. 4. The real $\chi'(\omega)$ and imaginary $\chi''(\omega)$ parts of the susceptibility of interacting particles with (a),(b) $\chi_L = 0.2$; (c),(d) $\chi_L = 0.5$; (e),(f) $\chi_L = 1$. All the graphs show the dynamic susceptibility at ac field amplitude $\xi = 0.1$, 2, 6, 8, 10, and 20. The points are from numerical calculations, while the solid lines are from the new theory (18)–(21).

of the interacting and noninteracting systems. When $\xi \leqslant 3$, the peak frequency for an interacting system is lower than for a noninteracting system. In this case, the decreases in peak frequencies signal the onset of dipolar nose-to-tail correlations and concomitant increase in the characteristic rotation time. For an interacting system at $\xi = 3$, the peak frequency is about 1, that is, the relaxation processes in the system are characterized by the Brownian rotation time τ_B of the noninteracting particles. This occurs due to a balance between the competing dipole-field and dipole-dipole interactions. At

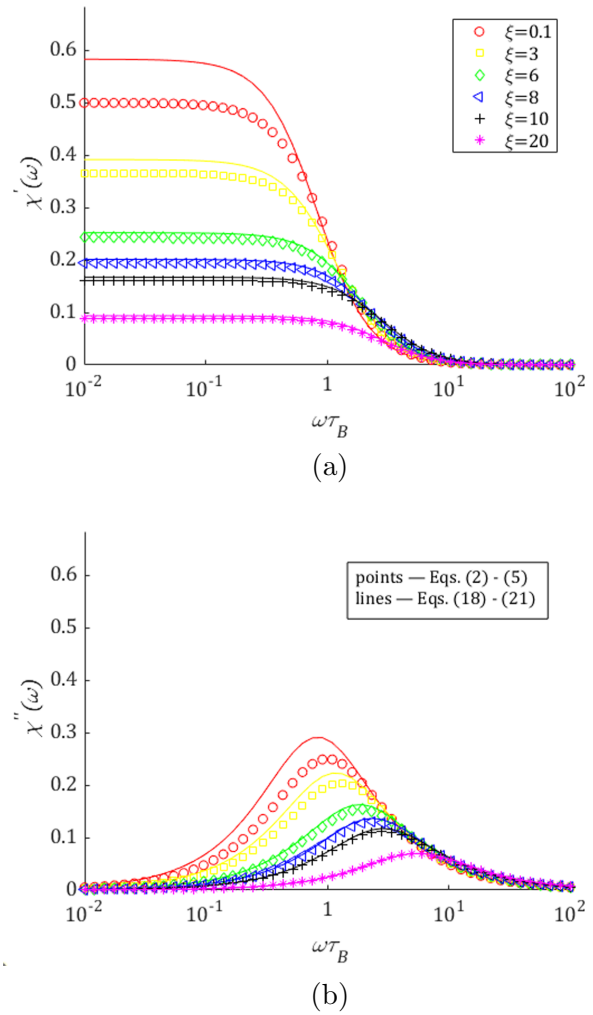

FIG. 5. The real $\chi'(\omega)$ (a) and imaginary $\chi''(\omega)$ (b) parts of the susceptibility of interacting particles with $\chi_L = 0.5$ at ac field amplitude $\xi = 0.1$, 3, 6, 8, 10, and 20. The points are from the Yoshida and Enpuku theory [23] [Eqs. (2)–(5) in this paper]. The solid lines are from the new theory [Eqs. (18)–(21)].

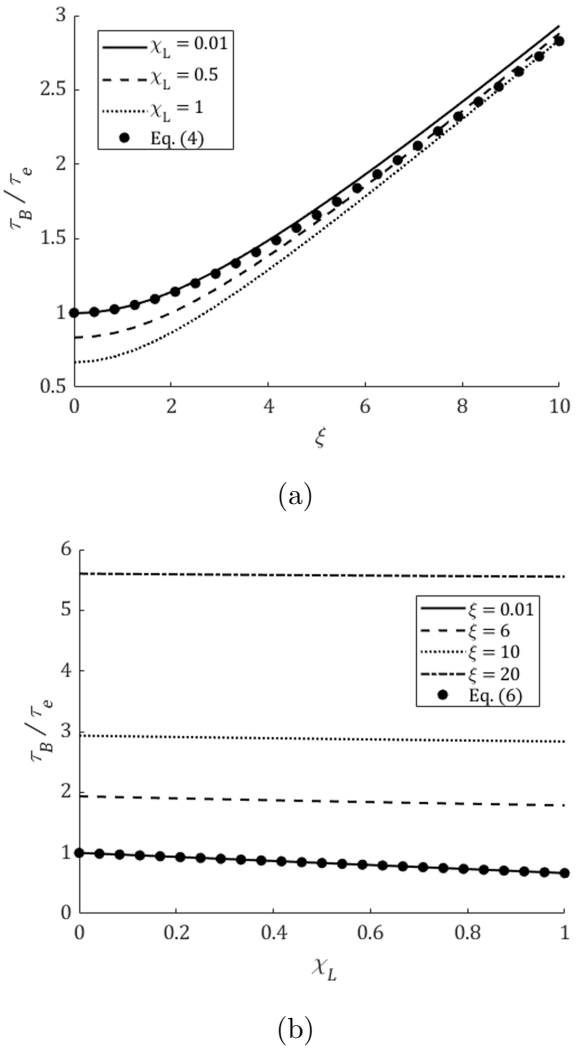

FIG. 6. The ratio τ_B/τ_e as a function of (a) ac field amplitude ξ, and (b) the Langevin susceptibility χ_L. The lines are from the new theory (20). The points are from the reference theories: (a) the Yoshida and Enpuku theory [23] for noninteracting particles [Eq. (4) in this paper]; (b) the Ivanov *et al.* theory [31] for interacting particles in a weak ac field [Eq. (6) in this paper].

$\xi = 0.01$, the peak frequency of interacting particles is less than 1: this is the effect of interparticle interactions. At $\xi \geqslant 6$, the peak frequencies are more than 1 and have almost the same value for both interacting and noninteracting particles at each value of ξ. This is because the dipole-field interaction dominates over the dipole-dipole interaction at a high-field amplitude.

Figures 6 and 7 show the peak frequency of the imaginary susceptibility and the low-frequency behavior of the real susceptibility in detail. The peak frequency characterizes relaxation processes. In an ideal system, the rotation of a particle is determined by Brownian rotation time $\tau_B = \pi\eta d^3/2k_BT$, which depends on particle size, temperature, and the viscosity of medium η. In the Debye theory, the maximum of the imaginary susceptibility is always achieved at the dimensionless frequency $\omega^*\tau_B = 1$. The intrinsic frequency of particle $1/\tau_B$ coincides with the frequency of the ac field ω^*, while the imaginary susceptibility demonstrates resonance. An increase in the amplitude of the ac field and/or interparticle interactions changes the characteristic relaxation time of the particle by effective time τ_e. In such systems, the maximum of the imaginary susceptibility is reached at $\omega^*\tau_e = 1$. Consequently, the peak frequency in the interacting system $\omega^*\tau_B = \tau_B/\tau_e$ clearly demonstrates a deviation of the effective relaxation time τ_e from the Brownian rotation time τ_B.

The lines in Fig. 6(a) show the ratio τ_B/τ_e as a function of the ac field amplitude ξ from the new theory (20). At $\chi_L = 0.01$, interparticle interactions are weak, so the new theory almost coincides with the case for noninteracting particles in Eq. (4) [points in Fig. 6(a)]. An increase in the field amplitude leads to a significant increase in τ_B/τ_e (about three times when ξ changes from 0 to 10). In contrast, an increase in the Langevin susceptibility at a constant field amplitude decreases τ_B/τ_e, which is more pronounced at low ξ. For systems with $\chi_L = 0.5$ and 1, the ratio τ_B/τ_e becomes equal to 1 at $2 \lesssim \xi \lesssim 3$, signaling the balance between the dipole-dipole interaction (which slows down the relaxation processes) and the field-

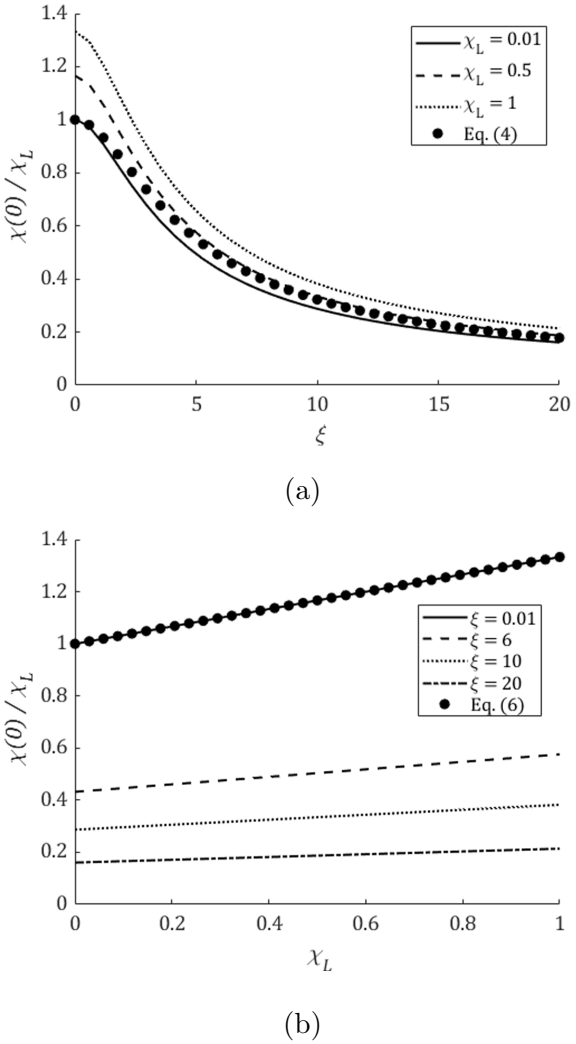

FIG. 7. Normalized real susceptibility at low frequencies $\chi(0)/\chi_L$ as a function of (a) ac field amplitude ξ, and (b) Langevin susceptibility χ_L. The lines are from the new theory (20). The points are from the reference theories: (a) the Yoshida and Enpuku theory [23] for noninteracting particles [Eq. (4) in this paper]; (b) the Ivanov *et al.* theory [31] for interacting particles in a weak ac field [Eq. (6) in this paper].

dipole interaction (which speeds them up). In the region of $\xi \gtrsim 8$, all lines are very close to each other, indicating that interparticle interactions affect relaxation processes weakly and that the field-dipole interaction mainly determines these processes. The influence of χ_L on the ratio τ_B/τ_e can be seen more clearly in Fig. 6(b), where the points are from reference theory [31] for interacting particles in a weak ac field.

The real susceptibility at low frequencies $\chi(0)$ is equivalent to the static field-dependent susceptibility. Figure 7(a) shows ratios $\chi(0)/\chi_L$ as functions of the ac field amplitude ξ. $\chi(0)/\chi_L$ decreases monotonically with increasing ξ. In the range $\xi \gtrsim 15$, the static susceptibility of interacting particles $\chi(0)/\chi_L$ almost coincides with the behavior of an ideal system (points in the plot) because the dipole-field interactions dominate over the dipole-dipole interactions. An alternative visualization of the same results is given in Fig. 7(b), which shows the static field-dependent susceptibilities as functions of the Langevin susceptibility χ_L. The theoretical results show that $\chi(0)/\chi_L$ increases as χ_L increases, but that the slope decreases with increasing field amplitude, due to the dipole-field interactions becoming more important than the dipole-dipole interactions. The points in Fig. 7(b) show the dynamic theory [31] for interacting particles in a weak ac field. It can be seen that the new theory is in good agreement with [31] for all values of $\chi_L \leqslant 1$.

IV. CONCLUSION

The new theory obtained on the basis of numerical calculations demonstrates the impact of dipolar interparticle correlations and the ac field amplitude on the dynamic susceptibility of ferrofluids. An increase in the ac field amplitude leads to the growth of dipole-field interactions. It was shown that the dipole-dipole and dipole-field interactions compete with each other, acting in the opposite way in relaxation processes and the magnetic response of the system to the ac field. There are two spectra characteristics that are especially sensitive to the influence of ac field amplitudes and dipole-dipole interactions: the low-frequency behavior of the real susceptibility, and the maximum of the imaginary susceptibility. Dipole-dipole interactions increase the low-frequency values of the real susceptibility, which characterizes the static magnetic response of the ferrofluid, while the ac field amplitude decreases them. The shift of the peak frequency of the imaginary susceptibility describes the relaxation processes in the system. Dipole-dipole interactions lead to a left shift of the maximum of the imaginary susceptibility from $\omega\tau_B = 1$, signaling an overall slowing-down of characteristic relaxation times and an increase in collective orientational dynamics. An increase in the ac field amplitude, on the contrary, speeds up relaxation processes. For some parameters, a balance between these interactions is reached, and the system exhibits the behavior of ideal noninteracting particles: in other words, the relaxation processes in the system are characterized by the Brownian rotation time.

The obtained approximate formulas for dynamic susceptibility predict the dynamic response of ferrofluids in a complex manner, taking into account simultaneously the influence of the ac field amplitude and dipole-dipole interactions. This result is especially important for medical applications, where the correct prediction of the working frequency range and the ac field amplitude defines the efficiency of treatment.

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