Amplitude Dependence of Dynamic Susceptibility of a Magnetic Fluid at Acoustic Frequencies

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Abstract. The energy dissipation in a magnetic fluid in the alternating magnetic field at the acoustic frequency was investigated experimentally. The purpose of the work is to gain information concerning the amplitude dependence of the dynamic susceptibility and the applicability range of the simplest linear relaxation equation for magnetization. Two independent methods were used: direct measurement of the dynamic susceptibility by a mutual inductance bridge in a weak sounding field and measurement of heat release in a magnetic fluid at high magnetic field amplitudes. In the latter case, the measuring technique is based on the well-known formula relating the heat release rate to the imaginary part of the dynamic susceptibility, which directly follows from the linear relaxation equation. A comparison of the results obtained by different methods revealed a systematic discrepancy between the results of two series of experiments, which is explained by the existence of multi-particle clusters (aggregates) in the magnetic fluid with uncompensated magnetic moments. At frequencies of about $10^4$ Hz, the brownian mechanism for the relaxation of magnetic moments is blocked due to the large size of the aggregates ($\omega \tau \gg 1$). In addition, at small amplitudes of the sounding field, the Neel relaxation mechanism is also blocked due to the high energy of inter-particle interactions inside the aggregate and the appearance of high potential barriers. The situation changes with an increase in the field amplitude, when the energy of interaction of the aggregated particles with the external field becomes comparable with the height of the potential barrier. The aggregates are involved in the process of magnetization reversal, increasing the dynamic susceptibility and energy dissipation in a magnetic fluid.

1. Introduction
Magnetic fluids — colloidal solutions of ferromagnetic nanoparticles in a carrier fluid — are typical representatives of superparamagnetic systems [1–4]. When the fluid is in the state close to a thermodynamic equilibrium, the magnetization dynamics of $M$ is well described by a linear equation [1–3]

$$\frac{dM}{dt} = -\frac{1}{\tau}(M - M_0)$$

(1)

where $M_0$ is the equilibrium magnetization, $\tau$ is the characteristic relaxation time. Since in weak fields the equilibrium magnetization is proportional to the magnetic field strength ($M_0 \propto \mu_0 H_0$, $\mu_0$ is the initial susceptibility), and equation (1) is linear, the dynamic magnetization will be proportional to the magnetic field strength. In the most general case of alternating, linearly polarized magnetic field $H = H_0 \exp(i\omega t)$, the solution of equation (1) can be written as

$$\vec{M} = (\chi_1 - i\chi_2)H_0 \exp(i\omega t)$$

where the real and imaginary parts of the dynamic susceptibility are defined by the Debye formulas [1, 5].
Obviously, the sum of all spectral amplitudes is nothing else but an initial particle interactions on the dynamics of magnetization has been the focus of several recent papers, the particle interactions, including the formation of aggregates, play a key role. Although the effect of inter-

\[ \chi_1 = \frac{\chi_0}{1 + \omega^2 \tau_i^2}, \quad \chi_2 = \frac{\chi_0 \omega \tau_i}{1 + \omega^2 \tau_i^2} \]  

The real part of the susceptibility \( \chi_1 \) determines the component of magnetization, which is in phase with the field strength, whereas the imaginary part \( \chi_2 \) is responsible for the dissipation of magnetic energy due to the alternating processes of the liquid magnetization reversal. The corresponding component of magnetization has a 90 degree lag from the phase of the field strength. According to [3, 5], the power dissipated in an arbitrary volume \( V \) of the magnetic fluid in a weak alternating magnetic field is determined by the formula

\[ Q = \mu_0 \omega \chi_2 V \frac{H_0^2}{2} \]  

where \( \mu_0 = 4\pi \times 10^{-7} \) H/m is the magnetic constant, \( \omega \) and \( H_0 \) are the cyclic frequency and amplitude of the alternating magnetic field, respectively.

A characteristic feature of real magnetic fluids is a wide spectrum of relaxation times associated with the polydispersity of single-domain particles, the existence of clusters and two independent mechanisms for the relaxation of the magnetic moment of a particle - the Brownian and Neel relaxation mechanisms [1, 6]. For this reason, formulas (2), corresponding to a system with the same relaxation time, are represented as the expansion in terms of the Debye function. The low-frequency part of the dynamic susceptibility spectrum we are interested in is well described by series with a relatively small \( N = 4 \ldots 7 \) number of terms, each of which corresponds to a separate fraction of particles (or clusters) with a fixed time \( \tau_i \) of the magnetic moment relaxation [6].

\[ \chi_1 = A_0 + \sum_{i=1}^{N} \frac{A_i}{1 + \omega^2 \tau_i^2}, \quad \chi_2 = \sum_{i=1}^{N} \frac{A_i \omega \tau_i}{1 + \omega^2 \tau_i^2} \]  

The spectral amplitudes \( A_i \) denote the contribution of the \( i \)-th "Brownian" fraction to the equilibrium susceptibility, and the first term in (4) describes the frequency-independent (at frequencies up to \( 10^5 \) Hz) contribution of the smallest particles, in which relaxation is governed by the Neél mechanism. Obviously, the sum of all spectral amplitudes is nothing else but an initial equilibrium susceptibility. If the fraction is represented by individual particles, the spectral amplitudes can be described by the well-known expression for the initial susceptibility of a magnetic fluid in the framework of the modified effective field model [7]:

\[ A_i = \frac{\mu_0 \langle m^2 \rangle n_i}{3kT} \left( 1 + \frac{\chi_L}{3} \right), \quad \chi_L = \frac{\mu_0 \langle m^2 \rangle n}{3kT} \]  

where \( n \) and \( n_i \) are the numerical densities of the particles for the system as a whole and for the specified fraction, respectively, \( m \) is the magnetic moment of the particle. Angular brackets denote averaging over the ensemble. According to (5), the spectral amplitude is proportional to the mean square of the magnetic moment, i.e. the sixth power of the diameter of the magnetic core of particles contained in the fraction. The appearance of clusters in a magnetic fluid does not lead to a qualitative change in the situation: the main contribution to the equilibrium susceptibility is by coarse fractions.

In the low-frequency limit, the quasi-equilibrium susceptibility does not depend on the field amplitude, if the Langevin parameter, corresponding to coarse particles, is sufficiently small. If we assume that the error of one percent is acceptable, then the corresponding condition is written as

\[ \xi = \frac{\mu_0 m H_0}{kT} \leq 0.3 . \]

For typical magnetic colloids this condition is fulfilled at the field amplitudes as high as 400–500 A/m [8] and is actually the condition for the realization of formula (5) for spectral susceptibilities \( A_i \). In the dynamic mode (\( \omega \tau_i \sim 1 \)), the relaxation times and their dependence on the field strength and inter-particle interactions, including the formation of aggregates, play a key role. Although the effect of inter-particle interactions on the dynamics of magnetization has been the focus of several recent papers, the
problem is still far from being solved [9]. The purpose of this work is to obtain an experimental estimate of the range of sounding fields, in which the dynamic susceptibility can be considered constant quantity, which is independent of the field amplitude, and formulas (4) can be used to calculate the energy dissipation in a magnetic fluid. From the viewpoint of applied problems, the work may be of special interest in connection with the ongoing attempts of using magnetic nano particles for hyperthermia of tumors [10, 11]. In particular, in [10], the emphasis is placed on the problems associated with the duration of the therapeutic procedure and control of tumor temperature. The development of solutions to both problems requires an appropriate selection of the frequency and amplitude of the alternating magnetic field and correct estimation of the maximum heat release rate.

2. Experiment details
To create a uniform magnetic field, a long solenoid with a length of \( L = 374 \text{ mm} \) and a diameter of \( D = 33 \text{ mm} \) \((L \gg D)\) was used. The solenoid was formed by winding an enameled wire (EWW) of a diameter of 0.31 mm on a tube made of polyvinylchloride. The number of turns is \( N = 1080 \). A test tube with a magnetic fluid was located axially in the middle part of the solenoid. The length of the test tube was 107 mm, and the internal diameter was 8 mm. The ends of the test tubes were tightened with plastic washers, the diameters of which coincide with the internal diameter of the tube. This prevents the shift of the tube inside the solenoid during measurements. To measure the strength of the solenoid current, the solenoid was connected in series to a non-inductive resistor \( R_1 = 1.05 \text{ Ohms} \). The half-period average voltage of the resistor was measured with a F5053 voltmeter. The solenoid was connected to an a. f. amplifier intended for receiving a sinusoidal signal from a low-frequency generator.

![Figure 1. Schematic representation of the solenoid and coordinate axis](image)

The magnetic field along the axis of the solenoid can be easily calculated by breaking the solenoid into thin rings and using the superposition principle (for example, [12]).

\[
H = \frac{IN}{L} \left( \frac{Z_1}{\sqrt{4Z_1^2 + D^2}} + \frac{L - Z_1}{\sqrt{4(L - Z_1)^2 + D^2}} \right),
\]

where \( N \) is the number of turns of the solenoid, \( I \) is the strength of the winding current, \( z \) is the distance from the ring plane to an arbitrary point \( Z_1 \) on the solenoid axis, at which the field strength is evaluated (Fig. 1). In the middle part of a long solenoid, formula (6) predicts the existence of a region with a uniform field \( H = \frac{IN}{L} \). In particular, for the above mentioned geometry of the solenoid, the field strength in the tube was quite correctly described by the formula \( H = \alpha I \), \( \alpha = (2.88 \pm 0.02) \times 10^3 \text{ m}^{-1} \), and the field heterogeneity did not exceed 1 %.

Temperature measurements were taken using a copper-constantan thermocouple, the hot junction of which was glued to the wall of the tube, and the cold one – to the inner wall of the solenoid. The EMF of the thermocouple was measured with a voltmeter SHCH–300.

In the experiments, we studied two samples of a typical magnetic fluid, which is a composition of magnetite particles suspended in kerosene and stabilized by the oleic acid. The sample densities were measured with a densitometer at room temperature. The volume fraction of the solid phase was estimated
by the formula $\varphi = \left( \rho - \rho_b \right) / \left( \rho_m - \rho_b \right)$, where $\rho_b = 0.78 \text{ g/cm}^3$ is the kerosene density at room temperature, and $\rho_m = 5.2 \text{ g/cm}^3$ is the magnetite density. The fluid viscosity was evaluated by the Chow formula [13]

$$\frac{\eta}{\eta_0} = \exp\left( \frac{2.5\varphi}{1-\varphi} \right) + \frac{A\varphi^2}{1-AP\varphi^2}. $$

Here, $A = 4.67$, $P = 0.605$ is the coefficient of particle packing, at which the fluid loses its fluidity, $\eta_0 = 1 \cdot 10^{-3} \text{ Pa} \cdot \text{s}$ is the viscosity of kerosene at room temperature. The operating frequency range was determined from the condition $\omega\eta_0 \sim 1$, where

$$\tau_B = \frac{\pi \eta d^3}{2kT}$$

is the Brownian relaxation time of the magnetic moments [4] corresponding to the fraction of colloidal particles with a hydrodynamic diameter $d = 15 \text{ nm}$ prevailing in the solution [6]. An estimate of the Brownian relaxation time gives $\tau_B \sim 10^{-5} \text{ s}$, which corresponds by the order of magnitude to the frequency of the sounding field $\nu = 10^{-16} \text{ kHz}$. For this frequency range, the dynamic effects should be most pronounced.

The most critical part of the measurements was finding the magnitude of the maximum rate of heat release $Q$ in the magnetic fluid. It was determined by the radial temperature difference in the gap between the wall of the tube and the wall of the solenoid. The relationship $\varepsilon(Q)$ between the EMF of a thermocouple and the rate of heat release $Q$ was derived from the calibration tests. For this purpose, we created a miniature electric heater, the dimensions of which allowed its location inside the test tube. Heater resistance was $R_2 = 8.13 \cdot 10^3 \text{ Ohm}$. As a power source we used a GPR–7550D model, whose effective voltage $U_2$ at the output terminals was measured with a GDM–8246 voltmeter (Fig. 2). Upon installation of the heater in the tube, the remaining space of the tube was filled with glycerin. The power of the heater was varied stepwise, and the stationary temperature regime was established within several tens of minutes after changing. To ensure maximum approximation of the calibration conditions to the conditions of magnetic fluid experiment, the alternating current passing through the coil of the solenoid was of the same strength as the current in real tests. Examples of calibration curves for two values of the solenoid current strength are shown in figure 3. As expected, the calibration curves are well approximated by a linear relationship.
Another systematic error in the calculation of the imaginary part \( \chi_2 \) of susceptibility was associated with its temperature dependence and the variation of the average temperature with a change in the frequency and amplitude of the field. To control the temperature of the magnetic fluid, an additional thermocouple was used. Its hot junction was in the liquid, and the cold one in a vessel with melting ice. The temperature coefficient \( \chi_2 \) was determined based on the results of measurements by the mutual inductance bridge in the limit of small amplitudes [8]. The dependence \( \chi_2(t) \) was approximated by a linear function \( \chi_2(t) = mt+c \). The results of the approximation are given in Table 1.

| \( \nu \), kHz | \( m \cdot 10^{-2} \), °C\(^{-1} \) | \( c \) |
|----------------|---------------------------------|------|
| 10.0           | -1.39                           | 0.920|
| 12.0           | -1.36                           | 0.917|
| 14.0           | -1.30                           | 0.911|
| 16.0           | -1.40                           | 0.950|

3. The results of measurements
The results of calculating the imaginary part of the dynamic susceptibility by formula (3) at higher magnetic field amplitudes (up to 1.3 kA/m) were compared with the results of measurements by a mutual inductance bridge at small amplitudes (up to 200 A/m) taking into account the corrections for temperature according to Table 1. The results of this comparison are shown in figure 4 for a sounding field frequency of 10 kHz. These results look very unusual, since an increase in the field amplitude would have led to a decrease in susceptibility due to a decrease in the spectral amplitudes. That was not the case. Moreover, there is even a slight increase of about 15% in the imaginary part of the susceptibility. In our opinion, such a behavior of the dynamic susceptibility is associated with two factors: the presence of nanoscale aggregates in the magnetic fluid with the Brownian mechanism for the relaxation of magnetic moments and the selected frequency range. At frequencies of the order of 10^4 Hz, the Brownian relaxation mechanism of aggregates is blocked because of their large sizes \( (\omega t_0 \gg 1) \). Moreover, at small amplitudes of the sounding field, the Neel mechanism of magnetization relaxation is also blocked due to the high energy of inter-particle interactions inside the aggregate. The magnetic moments of individual particles in an aggregate are not capable of overcoming the existing potential barriers, and the aggregate “is not involved” in the processes of magnetization reversal. The situation changes with an increase in the field amplitude, in which case the energy of interaction of the aggregated particles with the external field is comparable with the height of the potential barrier. The aggregates are included in the process of magnetization reversal, increasing the dynamic susceptibility.
and energy dissipation in the magnetic fluid. In the quasi–static mode ($\omega t_0 \ll 1$) the magnetization reversal occurs due to the Brownian rotation of the aggregates and the existence of potential barriers inside the aggregate does not affect the dynamics of the process.

Figure 4. The imaginary part of the dynamic susceptibility of magnetic fluid samples with $\phi = 0.13$ and $\phi = 0.17$, respectively, at a frequency of 10 kHz. 1’ – corresponds to the calculation by formula (3), 2’ – corresponds to the mutual inductance bridge measurements. The solid line shows the linear approximation of the results obtained from the mutual inductance bridge measurements.

4. Conclusion
In general, our results suggest that the dynamic effects associated with the unblocking of the Néel mechanism for the relaxation of magnetic moments inside the aggregates almost completely compensate for a decrease in the spectral amplitudes with decreasing strength of the sounding field, in compliance with equations (4). The contributions of separate terms in the right-hand side of (4) substantially depend on the field amplitude (at a fixed frequency), but their sum varies only slightly. As a result, the amplitude dependence of the dynamic susceptibility at the acoustic frequencies is very weak, and the range of magnetic fields, at which equation (3) is valid at the acoustic frequencies, can be extended at least to 1.3 kA/m.

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