JOURNAL OF NANO- AND ELECTRONIC PHYSICS *ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ*
Vol. **6** No 3, 03056(4pp) (2014) Том **6** № 3, 03056(4cc) (2014)

Features of the Rotational Kinetic of Magnetic Fluid Nanoparticles

A.M. Storozhenko[1,*], P.A. Ryapolov[1], A.O. Tantsyura[1], V.M. Polunin[1], I.M. Aref'ev[2], T.A. Aref'eva[2], Yu.B. Kazakov[2], Yu.A. Neruchev[3], V.I. Korotkovskii[3]

[1] *Southwest State University, Kursk, Russia*
[2] *Ivanovo State Power University named after V.I. Lenin, Ivanovo, Russia*
[3] *Kursk State University, Kursk, Russia*

(Received 19 May 2014; revised manuscript received 07 July 2014; published online 15 July 2014)

The results of theoretical and experimental studies of the effect of the perturbation of magnetization of magnetic fluid in the initial part of magnetization curve, caused by thermal oscillations in the adiabatic sound wave are considered. The measurements were carried out on the magnetic colloid samples with different viscosity of the dispersion medium within the frequency band of 20-60 kHz. In this frequency band, studied samples are characterized by the absence of thermal relaxation of the magnetization. The comparison of the conclusions of the model of thermal relaxation of magnetization and the experimental results makes it possible to obtain information about the features of the rheology for the nearest molecular environment of a particle – nanorheology.

Keywords: Magnetic fluid, Acoustomagnetic effect, Relaxation of magnetization, Magnetic nanoparticle, Magnetization curve.

PACS numbers: 62.80. + f, 43.35. + d

1. INTRODUCTION

Magnetic fluids (MF) are stable systems of magnetic nanoparticles in a carrier liquid [1]. They are widely used in various branches of engineering [2-3]. Structure of real MF is studied by methods of acoustic spectroscopy [1, 4-6], Magneto-granulometric analysis [7], Magnetorelaxometry (MRX) [2], Acousto-granulometric analysis [8] and others.

Data on the rheology of the nearest molecular environment of magnetic fluid nanoparticle can be obtained by analyzing the initial part of the curve of acoustomagnetic effect (AME) [9]. AME curve is a dependence of the relative amplitude of e.m.f. in the coil on the magnetic field voltage [1].

The aim of this paper is testing the proposed method on a series of MF-samples with different carrier liquids. The subject of study is the effect of the perturbation of the magnetization of a magnetic colloid caused by ultra-low thermal vibrations in the adiabatic sound wave, and its relaxation.

2. THEORETICAL BASIS

The equation of acoustomagnetic effect for low-concentration MF is

$$\Delta M / \Delta M_{\max} = (M_0 / M_S) \times \times \left[\left(1 + \gamma_* M_T / M_0\right) \left[\left(1 + N_d M_H\right) \right]^{-1} + \left(\omega\tau\right)^2 \right] / \left[1 + \left(\omega\tau\right)^2 \right] \quad (1)$$

where $\Delta M / M_{max}$ is relative increment in the amplitude of the magnetization, M_0 is the magnetization of the medium in the unperturbed state, M_T is the temperature magnetization coefficient, M_H is the magnetic susceptibility, N_d is the dynamic demagnetization factor [10], $\gamma_* = qTc^2/C_p$, q is the thermal expansion coefficient, T is the absolute temperature, c is the sound speed in the MF, C_p is the specific heat capacitance at constant pressure, ω is the circular frequency of oscillation, $\tau \equiv \tau_1(1 + N_d M_H)^{-1}$ is the relaxation time of the magnetic moment.

The initial part of AME curve is a linear dependence on magnetic field voltage [11-12]. Its angular coefficient is

$$\mathrm{tg}\,\theta_A = (\chi / M_S) \left[\left(1 + k' \frac{T}{\chi} \cdot \frac{\partial \chi}{\partial T} \right) \left(1 + N_d \chi\right)^{-1} + \left(\omega\tau\right)^2 \right] \times \times \left[1 + \left(\omega\tau\right)^2 \right]^{-1} \quad (2)$$

where χ is initial magnetic susceptibility of MF, $k' = qc^2/C_p$.

The expression (2) can be used for comparing with the experimental results in frequency band, which includes the area of thermal relaxation of the magnetization.

With respect to low-concentration MF in monodispersed approximation it is possible to use a well-known generalization of Langevin theory of paramagnetism for superparamagnetics [3, 13]:

$$\chi = \frac{\mu_0 M_S m_*}{3k_0 T} = \frac{\mu_0 n m_*^2}{3k_0 T}, \quad (3)$$

where m_* is the magnetic moment of a nanoparticle, n is the volume concentration, μ_0 is the magnetic constant, k_0 is the Boltzmann constant.

After the substitution of (3) for (2), we obtain

$$tg\theta_A = \frac{\mu_0 m_*}{3k_0 T} \cdot \frac{\frac{1 - k'}{1 + k''/3} + (\omega\tau)^2}{1 + (\omega\tau)^2}, \quad (4)$$

* storogenko_s@mail.ru

The article was reported at the International Conference «The Advanced Technology, Equipment and Analytical Systems for Materials», Kursk, 13-14 May, 2014

where $k'' = \frac{N_d \mu_0 n m_*^2}{k_0 T} = \frac{N_d \mu_0 M_S m_*}{k_0 T}$ [14].

The obtained expression (4) contains the dependence of $\mathrm{tg}\theta_A$ on the frequency of sound oscillations ω and the thermal relaxation time of the particle magnetization τ.

From the formula (4) we obtain $\mathrm{tg}\theta_2$ which is the angular coefficient of the initial part of AME-curve when $N_d = 0$, $k'' = 0$

$$tg\theta_2 = \frac{\mu_0 m_*}{3k_0 T} \cdot \frac{1 - k' + (\omega\tau)^2}{1 + (\omega\tau)^2}, \qquad (5)$$

the expression for $\mathrm{tg}\theta_3$ when $(\omega\tau)^2=0$

$$tg\theta_3 = \frac{\mu_0 m_*}{3k_0 T} \cdot \frac{1 - k'}{1 + k''/3} = \frac{\mu_0 m_*}{k_0 T} \cdot \frac{1 - k'}{3 + k''}, \qquad (6)$$

the expression for $\mathrm{tg}\theta_4$ when $(\omega\tau)^2 >> 1$

$$tg\theta_4 = \frac{\mu_0 m_*}{3k_0 T}. \qquad (7)$$

Henceforward, the conclusions of the model theory of thermal relaxation in the form of the formulas (4)-(7) will be we compared with the experimental results.

3. DECRIPTION OF THE OBJECTS AND METHODS OF RESEARCH

The samples of magnetic fluids on the high-dispersive magnetite Fe_3O_4 basis stabilized with oleic acid $C_8H_{17}CH{=}CH(CH_2)_7CO{-}O^-H^+$ in different carrier liquids were studied during the experiment:

- Sample MF-1, the carrier is kerosene;
- Sample MF-2, the carrier is Polyethylsiloxane-2;
- Sample MF-3, the carrier is mineral hydrocarbon oil;
- Sample MF-4, the carrier is Polyethylsiloxane-4;
- Sample MF-5, the carrier is synthetic hydrocarbon oil.

These samples were supplied by the scientific research laboratory of Applied ferrohydrodynamics of Ivanovo State Power Engineering University. The samples have similar magnetic properties: saturation magnetization and initial magnetic susceptibility; these make it possible to determine the potential influence of the carrier liquid properties on time of thermal relaxation of the MF magnetization.

The physical parameters of the MF samples are shown in Table 1. The following notations are used: density ρ, volume concentration of the solid phase φ, volume concentration of the magnetic phase φ_M, initial magnetic susceptibility χ, saturation magnetization M_S, sound speed c in the "MF-glass tube" system, thermal expansion coefficient q, specific heat capacitance at constant pressure C_p, plastic viscosity η.

The parameters ρ, q and C_p were determined experimentally in the laboratory of molecular acoustics of Kursk State University at the Department of General Physics [15].

For the MF test samples the time of the Brownian rotational diffusion of colloidal particles was determined according to $\tau_B = 3V\eta_{S0} / k_0 T$, where V is the volume of the particle, η_{S0} is the static shear viscosity of the carrier liquid. τ_B for the samples is MF-1 $\tau_B = 2$ μs, MF-2 $\tau_B = 6$ μs, MF-3 $\tau_B = 21$ μs, MF-4 $\tau_B = 26$ μs, MF-5 $\tau_B = 46$ μs.

The frequency-field dependence of the AME was studied using research facility in the Nanoscale acoustics laboratory of Southwest State University. The detailed descriptions of the research facility block scheme and the experimental techniques are given in [8, 11]. Magnetic parameters χ and M_S are calculated on the basis of the magnetization curves $M(H)$ obtained in the same laboratory using ballistic method [1].

4. RESULTS

For getting the features of the rheology for the nearest molecular environment of a particle we compared theoretical conclusions with the experimental data. For all the studied MF samples the dependence of the relative amplitude of the AME on the value of the magnetic field within the frequency band of 20-60 kHz were obtained.

We compared theoretical values of angular coefficients of initial parts of AME-curves with experimental results. Fig. 1 shows the plots, constructed using formulas (4)-(6), of the dependences of the tangent of the angle of inclination of the initial parts of the AME curves on frequency (lines) and the corresponding experimental data (points). The line $\mathrm{tg}\theta_1$ corresponds to formula (4), line $\mathrm{tg}\theta_2$ has been constructed using formula (5) taking into account $N_d = 0$, and line $\mathrm{tg}\theta_3$ has been constructed using formula (6) under the condition $(\omega\tau)^2 = 0$.

Calculation using expression (7) within the limits of an infinitely large thermal relaxation time gives us the following numerical values of the tangent of the angles of inclination: 0.080, 0.072, 0.078, 0.075, and 0.070, respectively, for samples MF-1, MF-2, MF-3, MF-4, and MF-5.

The values of magnetic moments of the nanoparticles m_* were calculated according to expression (3). We also used values τ_B and values of the dynamic demagnetizing factor N_d which were obtained experimentally in the frequency band of 10-60 kHz in [10].

We can state that the dependence $\mathrm{tg}\theta_3(\nu)$ corresponds the most to the experimental data. In this case, the chief criterion is the inclination of the theoretical

Table 1 – Physical properties of the samples under study

	ρ, kg/m³	φ, %	φ_M, %	χ	M_s, kA/m	c, m/sec	q, 1/K	C_p, J/kgK	η (Pa·sec)
MF-1	1252	10,6	8,5	2,8	35	937	0,00091	1489	0,012
MF-2	1385	10,3	8,3	2,5	34	930	0,0007	1375	0,125
MF-3	1282	10,3	8,2	2,6	34	1005	0,00082	1283	0, 368
MF-4	1405	10,2	8,2	2,6	34	954	0,00069	1326	0, 630
MF-5	1290	10,4	8,3	2,4	33	1024	0,00082	1284	1,110

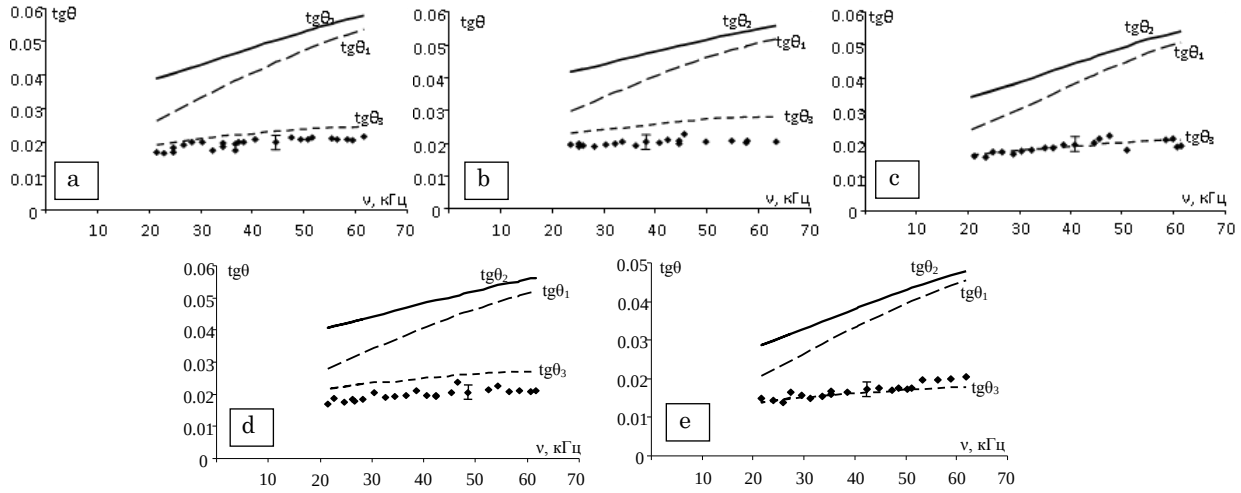

Fig. 1 – The theoretical and experimental values of tgθ: sample MF-1 (a); sample MF-2 (b); sample MF-3 (c); sample MF-4 (d); sample MF-5 (e)

curve toward the frequency axis. As concerns a certain displacement of dependences $\mathrm{tg}\theta_3(\nu)$ along the Y-axis relative to the trend of the experimental values, it may be the result of proximity of the parameter values entering into k' and k'', e.g., the m_* values obtained from the single particle approximation.

The correspondence between experimental data and theoretical results calculated according to the formula (6) indicates the absence of the thermal relaxation of the MFs magnetization in the initial part of the field dependence of AME in the frequency band of 10-60 kHz.

The "relaxation frequency" values of $\nu_R \equiv 1/2\pi\tau_B$ for the samples MF-1, MF-2, MF-5, MF-3, and MF-4 are 80 kHz, 27 kHz, 7.6 kHz, 6.1 kHz and 3.5 kHz respectively. Therefore, if $\omega\tau_B \approx 1$ is considered as the criterion of the thermal relaxation of the magnetization, then for the MF test samples (except sample MF-1) in the frequency band of 20-60 kHz this phenomenon should have been confirmed experimentally.

Nevertheless, what experimentally confirmed is the hypothesis according to which thermal relaxation is absent in the studied colloids, which is "low-probable" from the viewpoint of notions on rotational Brownian particle diffusion in a Newtonian fluid.

Thus, the fact of the absence of the thermal relaxation of the magnetization in relation to the values of the slope of the initial parts of the curves of the magnetization and the acoustomagnetic effect was experimentally obtained. Consequently, the surrounding environment of the nanoparticle in this case exhibits the properties of non-Newtonian fluid, which is characterized by special relations between the strain rate and stress.

The shearing strain of the medium, caused by the rotational oscillations of the nanoparticles, can be described by the Maxwell model, which is well-known in the viscoelastic media theory [16, 17]. The Maxwell mechanical model consists of a series-connected spring and piston (Fig. 2). In this case, the medium strain in the neighborhood of a nanoparticle is composed of two parts. The first part is instantaneous elastic strain, which is characterized by the shear modulus G. The second part is retarded viscous strain caused by me dium flotation, characterized by the shearing viscosity η.

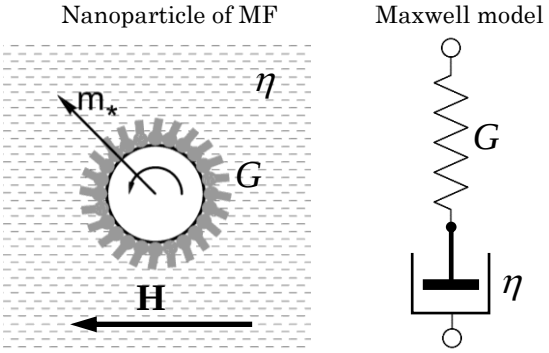

Fig. 2 – The offered model

The monomolecular layer of the stabilizer serves as an elastic component in the model under study, and the circumambient dispersion medium serves as a damper. Besides, neighboring particles of the disperse phase can retard the establishment of the equilibrium orientation of the magnetic moment of a particle. This occurs due to steric interaction.

The isolation of the elastic properties of the stabilizer coating has physicochemical nature: a molecule of the oleic acid on its polar end O^-H^+ is attracted to the solid phase surface forming thereon a dense unimolecular film of $\delta \approx 2$ nm thickness. Relatively closely-packed molecular structure of the stabilizer causes predominantly elastic shear strain of the coating which is characterized by short relaxation time. Considerable viscosity of the dispersion medium blocks the flotation processes at low rotational oscillations of nanoparticles. "Instantaneous" shear strain of the stabilizer coating under ultra-low temperature oscillations provides significant decrease of the values of the thermal relaxation time of the magnetization τ compared to the Brownian rotational relaxation time τ_B.

5. CONCLUSION

The comparison of the conclusions of the model of thermal relaxation of magnetization and the experimental results makes it possible to obtain information

about the features of the rheology for the nearest molecular environment of a particle − nanorheology.

The process of the magnetization perturbation of magnetic fluid caused by ultra-small thermal oscillations in a sound wave is largely determined by the rotational mobility of magnetic nanoparticles; the last one is determined by the viscoelastic properties of the medium. In this regard, the researches carried out in this direction are of great interest.

However, from both the experimental and theoretical point of view there are problems with the reliability of the obtained results and their interpretation. In respect to experiments the study of MF samples with low concentrations, as well as the displacement of the lower boundary of the magnetic force band to the area of small values are of great interest. From the theoretical perspective, there is a problem of developing a theoretical model which takes into account the polydispersity of the system and the interparticle interaction.

ACKNOWLEDGMENT

We are grateful for funding of this work via theGrant of the President of the Russian Federation for support of young researchers №14.Z56.14.5515-МК "The Development of an integrated methodology of acoustomagnetic researching of composition and structural parameters of magnetic nanoparticles in ferrofluids and ferrosuspensions".

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