VISCOUS AND THERMAL EFFECTS ON ACOUSTIC PROPERTIES OF FERROFLUIDS WITH AGGREGATES

R. BĂDESCU[1], G. APREOTESEI[1], V. BĂDESCU[2]

[1]Technical University "Gh. Asachi", Department of Physics, Blvd. Mangeron 56, Iasi 700050, Romania, E-mail: gabiap03@yahoo.com
[2]National Institute of Research and Development for Technical Physics, Blvd. Mangeron 47, Iasi 700050, Romania, E-mail: bav08@phys-iasi.ro

Received January 29, 2009

We present the expressions for the propagation velocity and for absorption coefficient of ultrasound in ferrofluids with aggregates. These make evident the viscous and thermal effects of oscillating and pulsating aggregates. Our numerical data give qualitative information on the ultrasound propagation in ferrofluids with fluid aggregates in the absence of a magnetic field.

Key words: ferrofluid, aggregate, suspension, ultrasound propagation, multiphase flow.

1. INTRODUCTION

Ferrrofluids are stable colloidal suspensions of ultrafine particles (~ 10 nm) of ferro- and ferrimagnetic materials in carrier liquids such as hydrocarbons, esters, water etc. [1, 2]. These fluids have the usual properties of liquids but in addition behave in the manner expected of an intrinsic liquid ferromagnet, *i.e*. they move as a whole in the direction of highest magnetic field and retain their liquid properties in the most intense magnetic fields.

Within the last years, an increasing attention was paid to the study of the ultrasound propagation through ferrofluids [3–10]. The experimental data now existing are yet quite contradictory, which can be explained by the different technologies used to prepare the ferrofluids and by their different nature. The existing theoretical works try to explain the peculiarities of ultrasound propagation through ferrofluids analyzing more physical mechanisms. Considering ideal ferrofluids (without aggregates), the electromagnetic, magnetocaloric, magnetostatic and magnetostrictive mechanisms are analysed [11–13], their contributions being only of the order of 10^{-2} m/s for the propagation velocity and of the order of $10^{-3} \div 10^{-1}$ m^{-1} for the attenuation coefficient.

Admitting that most ferrofluids contain aggregates of micronic sizes [13, 14] that appear when applying a magnetic field and persist a longer or shorter time after

canceling the field, we consider that the main mechanisms that determine the ferrofluids acoustic properties are the thermal mechanism (associated to the heat exchange between the aggregates and the carrier fluid) and the viscous mechanism (associated with the relative displacement of the aggregates with respect to the carrier fluid). We are only analyzing the ultrasound propagation in the ferrofluids with micronic aggregates in the absence of a magnetic field. In this case we consider the aggregates as spherical fluid particles dispersed in a carrying, more diluted ferrofluid, their density, viscosity and compressibility being influenced by the volume fraction of the solid colloidal particles they are made of. The results we have obtained give qualitative information preceding the study of ultrasounds propagation in ferrofluids in the presence of an applied magnetic field.

In Section 2 we present the acoustic wave equation derived by replacing the ferrofluid with aggregates by an equivalent homogenous and continuous fluid. In Section 3 we present the acoustical properties of ferrofluids with aggregates, namely, sound velocity and attenuation coefficients, extracted from the previously formulated wave equation. From this one can separate terms, each denoting the effects of thermal and viscous mechanisms, respectively, in the ultrasound propagation in the analysed system. In Section 4 we present some numerical applications made for ferrofluids based on kerosene, magnetite and oleic acid. The thermal and viscous contributions to the propagation velocity and to the attenuation coefficient are calculated as functions of the ultrasound frequency (in the range 1 ÷ 50 MHz) and of the ferrofluids density (in the range 850 ÷ 1100 kg/m^3). As parameters we take the size of the magnetite colloidal solid particles, the fraction of the solid particles within the system included in the aggregates and the packing factor of these in aggregates.

2. THE WAVE EQUATION

As an acoustic wave is passed through this system, the aggregates pulsate (radial expand and contract) and oscillate (move to and fro) relative to the suspending, more diluted, ferrofluid. An oscillating aggregate experiences a complex drag force, that is, a force which is the sum of the viscous and inertial parts. In a previous work [15] we have shown that the inertial part contributes to the sound velocity and the viscous part to the dissipation of the sound energy in the viscous layer near the aggregate boundary. When the aggregate performs pulsation, on account of different thermodynamic properties of system components, the temperature fluctuation of each component is different and heat is conducted between them in the thermal layer near the aggregate boundary. The system compressibility becomes a complex quantity. Since it enters the equation of

continuity and thereby the wave equation *via* the (assumed) linear relationship between the density fluctuation and acoustic pressure in system, its real part, which is larger than the volume averaged value of compressibility, contributes to the sound velocity, and its imaginary part determines the thermal attenuation of sound energy.

Let a plane acoustic wave of angular frequency ω be propagated through the ferrofluid with aggregates along the positive *x* direction. A cubical volume element with edges equal to 1/15 of the wave length λ at 1 MHz is about 10^{-6} cm^3. A ferrofluid for which the aggregates have the radius R=1 μm [16] and the volume fraction $\Gamma = 1\%$ will have in this volume about 2500 aggregates. In the absence of sound field it can be replaced, in the first approximation, by a homogeneous and continuous fluid of time and space independent volume averaged compressibility and density, of equilibrium values $\beta_v = \Gamma\beta_a + (1-\Gamma)\beta_f$ and $\rho_v = \Gamma\rho_a + (1-\Gamma)\rho_f$, respectively. In the previous relations and from now on the subscript a denotes the aggregate specific magnitudes, and the subscript f denotes the carrying fluid specific magnitudes.

In the presence of sound field, the specific magnitudes of the homogeneous and continuous fluid (equivalent to the ferrofluid with aggregates) fluctuate. Let these fluctuations (which for the plane wave are functions of *x* and *t* only), $\Delta\beta$ for the compressibility and $\Delta\rho$ for the density, be very small compared with their equilibrium values. $\Delta\beta$ arises by virtue of heat conduction between the ferrofluid components and $\Delta\rho$ arises by virtue of relative motion of these components. As a result of the differences between the thermodynamic properties of aggregates and that of carrying fluid, in a layer of thickness of the $\delta_t = \sqrt{2k_f/\rho_f C_{Pf}\omega}$ round of each aggregate will exist a temperature gradient. Here k_f is the thermal conductivity of the carrying fluid, and C_{Pf} is the specific heat at constant pressure. As a result of the temperature gradient, between the system components will exist a heat transfer and the fluid compressibility in the thermal layer becomes a complex quantity. Considering this, for the ferrofluid with aggregates compressibility in the presence of sound field we have found

$$\beta_s = \beta_v + \Delta\beta\,, \tag{1}$$

where

$$\Delta\beta = \beta_f \left\{ \left(\frac{3}{2}\Gamma\right)(\gamma_f - 1)\left(1 - \frac{\alpha_a \rho_f C_{Pf}}{\alpha_f \rho_a C_{Pa}}\right)^2 \left(\frac{\delta_t}{R}\right) + \right.$$
$$\left. + i\left(\frac{3}{2}\Gamma\right)(\gamma_f - 1)\left(1 - \frac{\alpha_a \rho_f C_{Pf}}{\alpha_f \rho_a C_{Pa}}\right)^2 \left(\frac{\delta_t}{R}\right)\left(1 + \frac{\delta_t}{R}\right) \right. , \tag{2}$$

α being the coefficient of the thermal expansion, $\gamma_f = C_{Pf}/C_{Vf}$, and $i = \sqrt{-1}$.

Assuming also that, in the first approximation, the linear relationship between the density and pressure fluctuations, that is true in a loss-free medium, is also true in the ferrofluid with aggregates, for the system density in the presence of sound wave we have found

$$\rho_s = \rho_f \left\{ 1 + \Gamma \frac{\left(\rho_{a,f} - 1\right)\left[\left(\rho_{a,f} + \tau\right)\left(1 + \tau\right) + \tau^2\right]}{\left(\rho_{a,f} + \tau\right)^2 + \sigma^2} + i\Gamma \frac{\left(\rho_{a,f} - 1\right)^2 \sigma}{\left(\rho_{a,f} + \tau\right)^2 + \sigma^2} \right\}, \tag{3}$$

where $\rho_{af} = \rho_a / \rho_f$. The magnitudes τ and σ in (3) enter inertial drag term and viscous drag term, respectively, of the complex drag force experienced by the oscillating viscous sphere, and are

$$\tau = \frac{1}{2} + \left\{ \left[\left(\frac{\delta_h}{4R} \right) \left(2 + 3\eta_{a,f} \right)^2 \right] \Big/ \left[\left(1 + \eta_{a,f} + \frac{R}{3\delta_h} \right)^2 + \left(\frac{R}{3\delta_h} \right)^2 \right] \right\}, \tag{4}$$

$$\sigma = \left(\frac{3}{4} \right) \left(2 + 3\eta_{a,f} \right) \left(\frac{\delta_h}{4R} \right)^2 \frac{\left[\left(1 + \frac{R}{\delta_h} \right) \left(1 + \eta_{a,f} + \frac{R}{3\delta_h} \right) + \frac{1}{3} \left(\frac{R}{\delta_h} \right)^2 \right]}{\left[\left(1 + \eta_{a,f} + \frac{R}{3\delta_h} \right)^2 + \left(\frac{R}{3\delta_h} \right)^2 \right]}, \tag{5}$$

where $\eta_{a,f} = \eta_a / \eta_f$, and $\delta_h = \sqrt{2\eta_f / \rho_f \omega}$ is the distance of relaxation of the shear wave in the vicinity of oscillating viscous aggregate.

Let k_s be the propagation constant in the homogeneous and continuous fluid with aggregates, in which both viscous and thermal losses occur. In analogy with a dispersive single-phase fluid, for this can be written

$$k_s = \frac{\omega}{c_s} + iX_s, \tag{6}$$

where c_s is the propagation velocity of ultrasound in the ferrofluid and X_s is the sum of the viscous and thermal coefficients. Using this, the wave equation can be written as

$$\frac{\partial^2 v}{\partial x^2} = \left(\frac{k_s}{\omega} \right)^2 \left(\frac{\partial^2 v}{\partial t^2} \right), \tag{7}$$

where $\left(k_s/\omega\right)^2 = \rho_s \beta_s$ and $v \propto \exp\left[i\left(k_s x - \omega t\right) \right]$.

3. THE PROPAGATION PARAMETERS

After introducing of (6) in (7), considering of (1), (2) and (5), performing usual mathematical operations, and ignoring of the terms that contain second or higher order of smallness (such as Γ^2, Γ^3 etc.), one obtain the propagation velocity

$$c_s \approx c_f \left\{ 1+\frac{1}{2}\Gamma\left(1-\beta_{a,f}\right)-\frac{1}{2}\Gamma\left(\rho_{a,f}-1\right)\frac{\left(\rho_{a,f}+\tau\right)\left(1+\tau\right)+\sigma^2}{\left(\rho_{a,f}+\tau\right)^2+\sigma^2}-\frac{3}{4}\Gamma\left(\gamma_f-1\right)\left(1-\frac{\alpha_a\rho_f C_{Pf}}{\alpha_f\rho_a C_{Pa}}\right)^2\left(\frac{\delta_t}{R}\right)\right\}, \tag{8}$$

and the absorption coefficient of the ultrasound in ferrofluids with aggregates

$$X_s = \left(\frac{\omega}{2c_f}\right)\Gamma\left\{\frac{\left(\rho_{a,f}-1\right)^2\sigma}{\left(\rho_{a,f}+\tau\right)^2+\sigma^2}+\frac{3}{2}\left(\gamma_f-1\right)\left(1-\frac{\alpha_a\rho_f C_{Pf}}{\alpha_f\rho_a C_{Pa}}\right)^2\left(\frac{\delta_t}{R}\right)\left(1+\frac{\delta_t}{R}\right)\right\}, \tag{9}$$

where c_f is the ultrasound propagation velocity in the carrier ferrofluid.

The last two terms from the (8) represent the viscous and thermal effects on ultrasound propagation velocity in ferrofluids with aggregates, respectively,

$$\Delta c_{viscous} \approx -\frac{c_f}{2}\Gamma\left(\rho_{a,f}-1\right)\frac{\left(\rho_{a,f}+\tau\right)\left(1+\tau\right)+\sigma^2}{\left(\rho_{a,f}+\tau\right)^2+\sigma^2}, \tag{10}$$

$$\Delta c_{thermal} \approx -\frac{3c_f}{4}\Gamma\left(\gamma_f-1\right)\left(1-\frac{\alpha_a\rho_f C_{Pf}}{\alpha_f\rho_a C_{Pa}}\right)^2\left(\frac{\delta_t}{R}\right). \tag{11}$$

Also from (9) one observe that X_s can be written as the sum of two terms, one representing the viscous effect and the other the thermal effect on the wave absorption in the analysed system

$$X_{viscous} = \left(\frac{\omega}{2c_f}\right)\Gamma\left\{\frac{\left(\rho_{a,f}-1\right)^2\sigma}{\left(\rho_{a,f}+\tau\right)^2+\sigma^2}\right\}, \tag{12}$$

$$X_{thermal} = \left(\frac{\omega}{2c_f}\right)\Gamma\left\{\frac{3}{2}\left(\gamma_f-1\right)\left(1-\frac{\alpha_a\rho_f C_{Pf}}{\alpha_f\rho_a C_{Pa}}\right)^2\left(\frac{\delta_t}{R}\right)\left(1+\frac{\delta_t}{R}\right)\right\}. \tag{13}$$

4. NUMERICAL RESULTS AND DISCUSSIONS

A stated in the beginning we concentrate our attention on ferrofluids based on kerosene, magnetite and oleic acid, like those more studied experimentally.

Particularly, in the case of these ferrofluids, having as carriers nonpolar liquids, between solid particles in suspension is achieved a steric repulsion by usually coating them with long chain molecules (~ 2 nm in length) possessing a polar group which adsorbs on the their surfaces. If the tails of the long chain molecules are compatible with the carrier, they repel one another and cause a repulsion between particles. This repulsion is due to two effects, sometimes called an osmotic effect caused by the high concentration of chains in the region of overlap and a volume restriction effect due to the loss of possible conformations in between the two particles. Nevertheless, in much of usually ferrofluids aggregate are present due to magnetostatic interaction between suspended particles.

We have thought the analysed system as a suspension of spherical fluid aggregates in a diluted ferrofluid. Each of them contain in his turn solid particles of radius r coated with a layer of stabilising agent of thickness *d*. The volume fractions of the coated solid particles in original ferrofluid (before the aggregates get formed) and in the carrier ferrofluid are ϕ_0 and ϕ_f, respectively. The parameters α_a/α_f, β_a/β_f, η_a/η_f, ρ_a/ρ_f, γ_f, k_f, C_{Pa}/C_{Pf} and Γ, which enter in the relations (8)–(13) depend of these volume fractions and of other three factors that are not easy to obtain for a given ferrofluid. The first one is the ratio between the volume of the dispersing agent adsorbed on a solid colloidal particle, and the volume of the particle. Here we present this ratio by $z=\left(1+d/r\right)^3$. The second factor on which the eight above mentioned parameters depend is the fraction q of the solid material within the ferrofluid included in aggregates, and the third is the volume fraction ϕ_a of the coated solid particles in aggregates. We have considered $z=2\,;3\,;\text{and}\,4$ (for *d*=2 nm, $r\approx 7.7$ nm; 4.5 nm; and 3.4 nm respectively), $q=10\%$ and 20%, and $\phi_a=0.45$ and 0.55 (corresponding to random packed spheres).

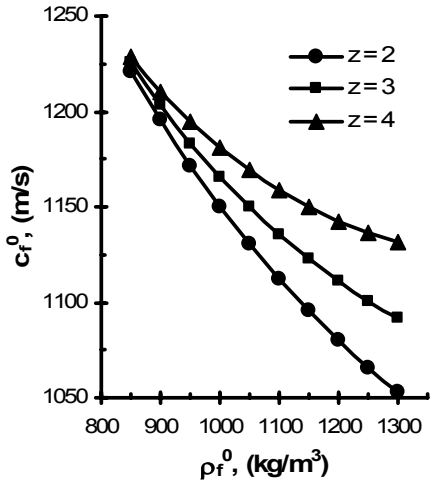

Fig. 1 – The dependence of propagation velocity of ultrasound in ferrofluids without aggregates on their densities and on sizes of magnetite colloidal particles.

For calculating of the ultrasound velocity in the carrier ferrofluid, we used the relation given by Polunin [17]:

$$c_f = \frac{c_0}{\sqrt{1+\phi_f\left(\frac{\rho_f}{\rho_0}-1\right)}\cdot\sqrt{1-\phi_f\left[1+(z-1)\left(1-\frac{\beta_d}{\beta_0}\right)\right]}}\cdot\left\{1-AT\phi_f\Big/1-\phi_f\left[1+(z-1)\left(1-\frac{\beta_d}{\beta_0}\right)\right]\right\}, \quad (14)$$

where

$$A=\frac{1}{2}(c_0)^2\,\rho_0\rho_p C_{Pp}\left(\frac{\alpha_p}{\rho_p C_{Pp}}-\frac{\alpha_0}{\rho_0 C_{P0}}\right)^2, \quad (15)$$

T is the absolute temperature (in our analysis $T=293$ K), and $c_0=\frac{1}{\sqrt{\rho_0\beta_0}}$ is the ultrasound propagation velocity in liquid base (in our analysis for kerosene at 293 K, $c_0=1250$ m/s). Figure 1 presents the density dependence of the propagation velocity in ferrofluids without aggregates, calculated according to (14). One can notice that for a given density, the propagation velocity increases when the colloidal solid particles sizes decrease. These numerical results are in accord with the experimental results in [10]. This effect results from the decrease of the volume fraction of the most compressible constituent (liquid base). With the obtained values and using known relations [17, 18, 19] for the material parameters entering in the relations (8)–(13) we calculated the ultrasound propagation velocity and the absorption coefficient for some hypothetical ferrofluids.

The appearance of the aggregates results in the increase of propagation velocity. In Figure 2 the relative increase is presented *vs.* the density of initial ferrofluid. One can see that this increase is the higher, the higher is the percentage of the colloidal solid particles included in aggregates and the larger are these particles. These numerical results are in accord with the experimental results concerning the effect of elapsed time from applying the magnetic field [9, 10]. This effect results from the increase of the difference between the densities of aggregates and carrying ferrofluid.

The dispersion in the propagation velocity within the range 5MHz ÷ 50 MHz is small, which has been also attested experimentally. It depends on the z, q and ϕ_a parameters (see Fig. 3) being the higher, the higher is the ratio between the aggregates density and carrying ferrofluid density. Qualitatively, these numerical results agree with the results of measurements carried out by varying the magnetic field intensity and frequencies [8]. These seem to be dependent on the characteristic time of Brownian motion of aggregates.

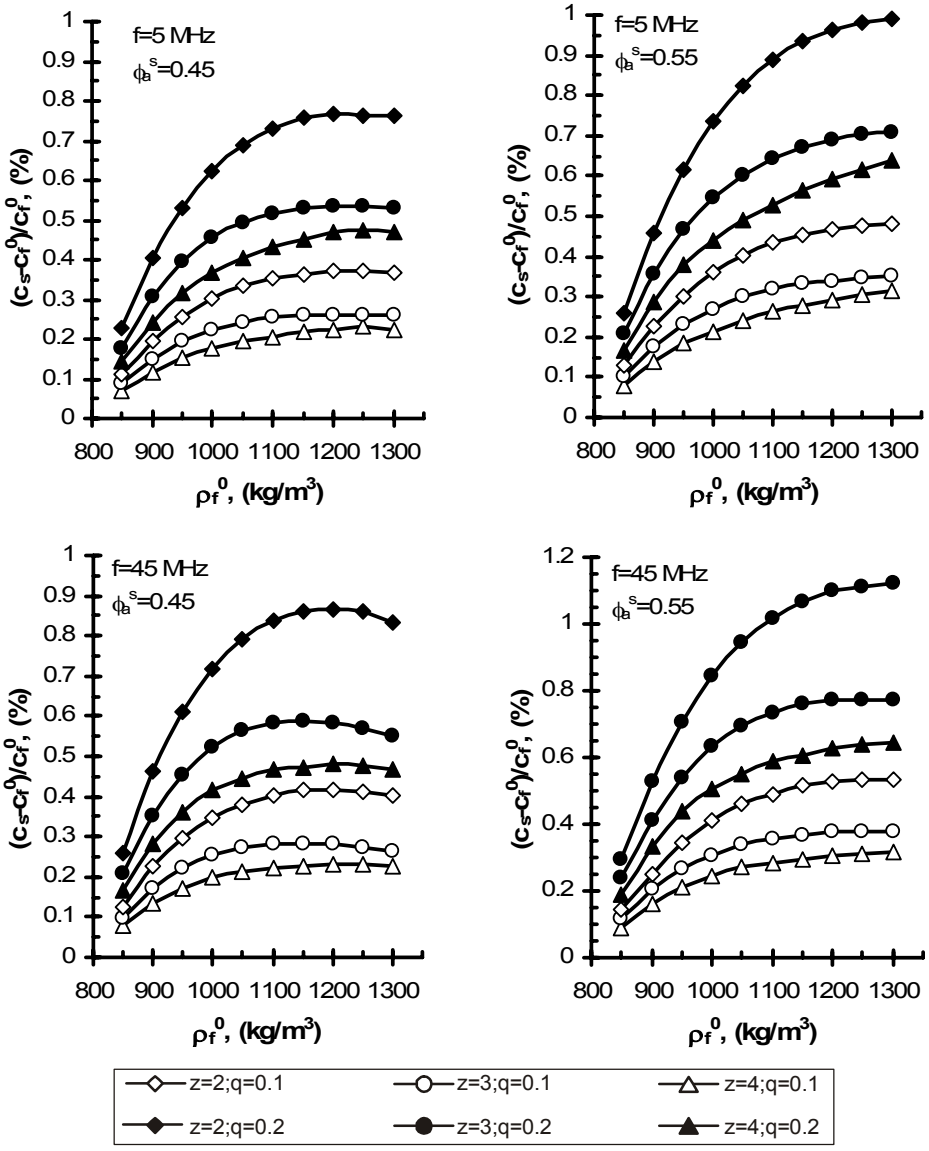

Fig. 2 – Relative increase of propagation velocity when aggregates appeared.

By evaluating the viscous and thermal effect of aggregates on the propagation velocity, we have noticed that the first one is of order 10 m/s, while the second one is negligible (~ 10^{-4} m/s). Both effects mainly depend on the initial ferrofluid density and the percentage of colloidal solid particles incorporated in aggregates. They are less influenced by the packing factor of colloidal solid particles in aggregates and by the ultrasound frequency (see Fig. 4).

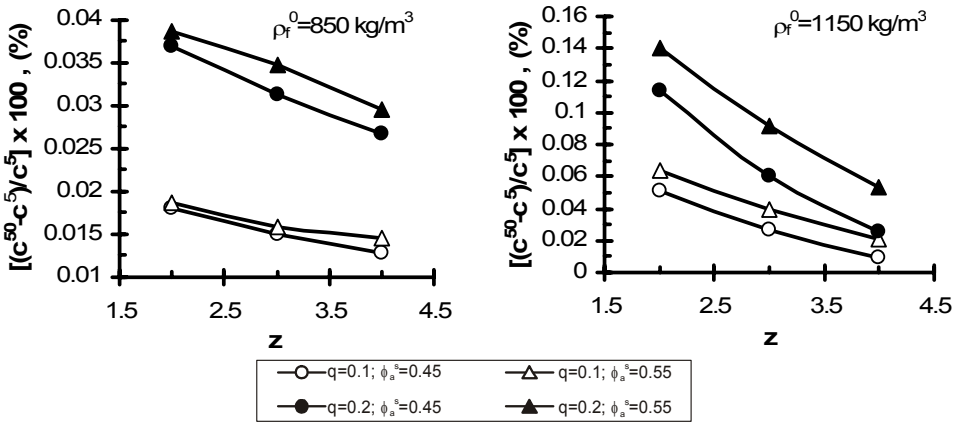

Fig. 3 – Dispersion of propagation velocity *vs.* structural parameters of some ferrofluids with fluid aggregates

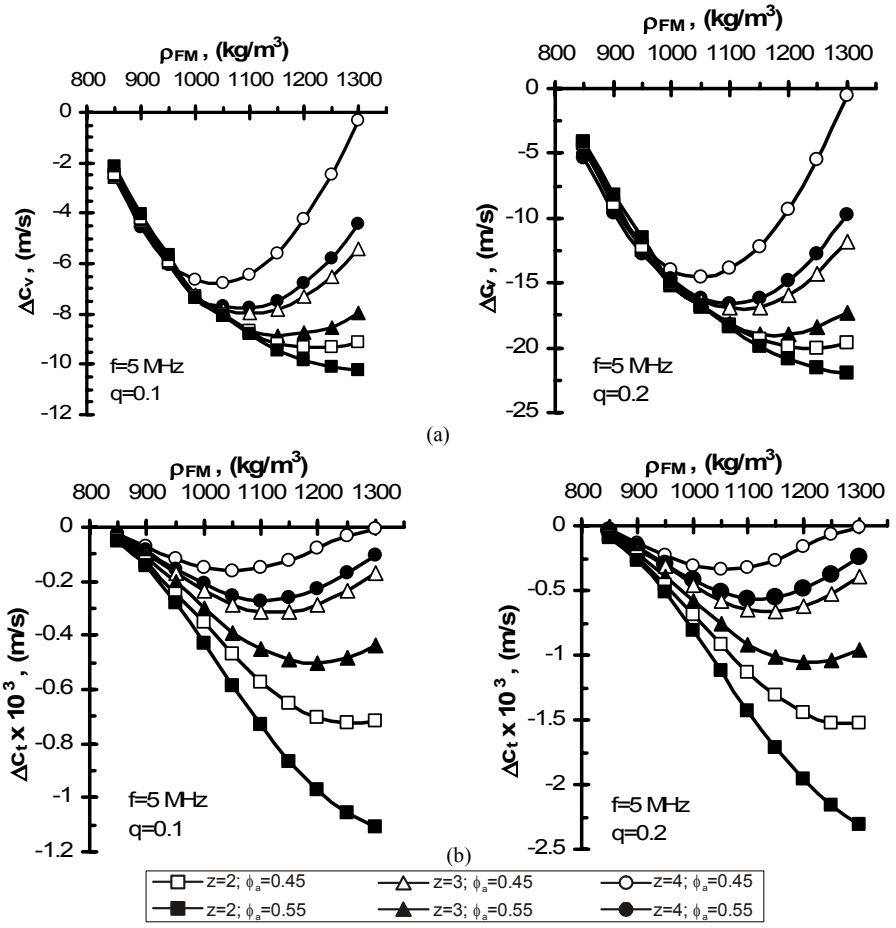

Fig. 4 – Viscous (a) and thermal (b) effects of oscillating fluid aggregates on propagation velocity.

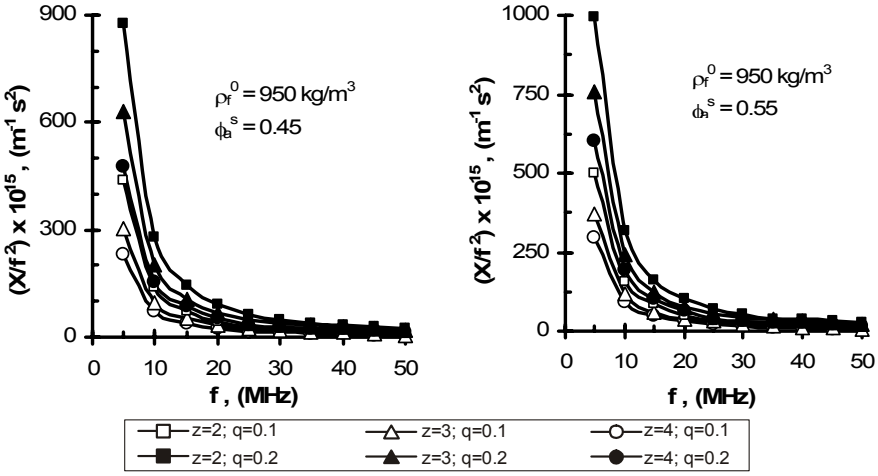

Fig. 5 – Attenuation of ultrasound in ferrofluids with aggregates, as X/f^2 *vs*. frequency.

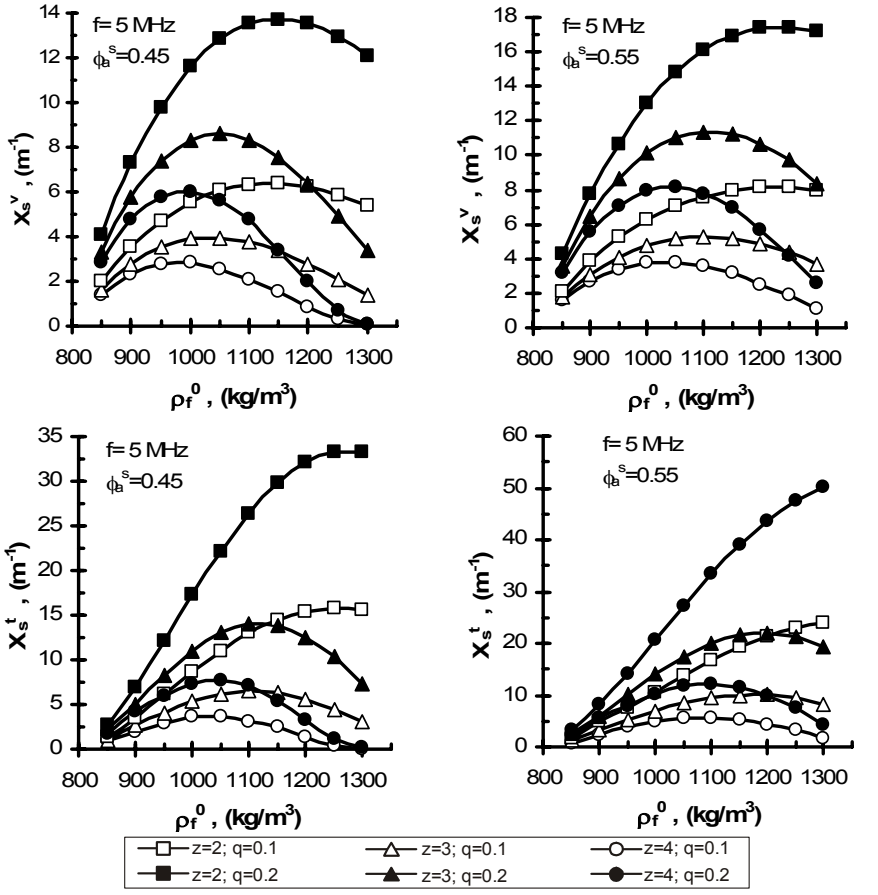

Fig. 6 – Attenuation of ultrasound in ferrofluids with fluid aggregates of different structural parameters *vs*. density of initial ferrofluids and *vs*. ultrasound frequency.

The ultrasound attenuation by the two effects is significant. Figure 5 presents the attenuation in terms of the ratio X/f^2. The fact that this ratio does not remain constant with increasing frequency proves the relaxation character of the attenuation, which also been established experimentally [7]. From this figure, the effect of the z, q and ϕ_a parameters on the ultrasound attenuation in aggregated ferrofluid is obvious. On the other side, the absorption coefficient increases with the initial ferrofluid density and with ultrasound frequency. It also increases with the percentage of colloidal solid particles incorporated in aggregates and with their dimensions, the numerical results being qualitatively in accord with the results of measurements concerning the effect of elapsed time from applying the magnetic field [9, 10]. In Figure 6 the dependencies of the absorption coefficient on the above parameters are presented for viscous and thermal effects. They are of the same order of magnitude and increase when the differences between the rheological and thermal characteristics of the aggregates and carrying ferrofluid get stronger.

5. CONCLUSIONS

We analysed only the ultrasound propagation in the ferrofluids with micronic aggregates in the absence of a magnetic field. The application of a magnetic field will first lead to aggregate extension. This effect results in the anisotropy of ultrasound propagation in relation with the field direction. Then the field determines both the change of the percentage of solid colloidal particles included in the aggregates, and the modification of the packing factor of these particles within the aggregates. These effects will result, in turn, in changes of elastic and rheological properties of aggregates which influences the acoustic parameters of the system. The dependence of these effects on the strength of applied magnetic field is not known until now.

Finally, we must underline that the values we obtained for the propagation velocity and absorption coefficient, as well as their dependencies on density and frequency are in qualitative agreement with many of the experimental results communicated in the literature.

REFERENCES

1. R.E. Rosensweig, *Ferrohydrodynamics,* Dover, Mineola, New York, 1997.
2. S. Odenbach, *Ferrofluids-magnetically controlled suspensions*, Colloids Surf. A: Physicochem. Eng. Aspects **217**, 171–178(2003).
3. K.Kh. Mansurov, V.V. Sokolov, *Acoustic properties of magnetic fluids. I. Kerosene-based magnetic fluids*, Magn. Gidrodin. **1**, 63–66 (in Russian)(1987).
4. M. Kaczmarek, T. Hornowski, A. Skumiel, *Ultrasonic waves in magnetic liquids: Two-phase approach and experimental results*, Acta Polonica **97**(4), 639–649(2000).

5. A. Skumiel, T. Hornowski, A. Józefczak, *Investigation of magnetic fluids by ultrasonic and magnetic methods*, Ultrasonics **38**, 864–867(2000).
6. A. Józefczak, A. Skumiel, M. Łabowski, *Effects of the sweep rate of the magnetic field on the changes of ultrasonic wave velocity in magnetic fluid*, J. Magn. Magn. Mater. **258–259**, 474–476(2003).
7. A. Józefczak, *Acoustic properties of PEG biocompatible magnetic fluid under perpendicular magnetic field*, J. Magn. Magn. Mater. **293**, 240–244(2005).
8. M. Motozawa, T. Sawada, *Influence of magnetic field on ultrasonic propagation velocity in magnetic fluids*, J. Magn. Magn. Mater. **289**, 66–69(2005).
9. M. Motozawa, T. Sawada, *Velocity and attenuation of ultrasonic propagation in magnetic fluids under a uniform magnetic field*, Int. J. Appl. Electromagnet. Mech. 28(1–2), 143–148(2008).
10. M. Motozawa, Y. Iizuka, T. Sawada, *Experimental measurements of ultrasonic propagation velocity and attenuation in a magnetic fluid*, J. Phys., Condens. Matter, **20**(20), Article Number 204117(2008).
11. K. Gotoh, W.E. Isler, D.Y. Chung, *Theory of ultrasound attenuation in magnetic fluids*, IEEE Trans. Magn. **MAG – 16**, 211–213(1980).
12. N.F. Patsegon, I.Ye. Tarapov, A.I. Fedonenko, *Application of ultrasonic techniques in studies of ferrofluid physical properties*, Magn. Gidrodin. **4**, 53–59 (in Russian)(1983).
13. K. Gotoh, D.Y. Chung, *Ultrasonic attenuation in ferrofluids*, IEEE Trans. Magn. **MAG – 16**, 251–253(1984).
14. J.-C. Bacri, D. Salin, *Dynamics of the shape transition of a magnetic ferrofluid drop*, J. Physique (Letters) **44**, L415–L420(1983).
15. R. Bădescu, E. Luca, V. Badescu, N. Rezlescu, *On ultrasound propagation parameters for magnetic fluids with aggregates*, Rom. Rep. Phys. **40**, 973–983(1994).
16. D.A. Krueger, *A review of agglomeration in ferrofluids*, IEEE Trans. Magn. **MAG – 16**, 251–253(1980).
17. V.M. Polunin, *Effect of internal heat exchange in a magnetic fluid on its elastic properties*, Magn. Gidrodin. **1**, 138–139 (in Russian)(1984).
18. M.I. Shlioms, *Magnetic fluids*, Sov. Phys. Usp. **17**, 153–169(1974).
19. V.M. Polunin, *Microinhomogeneity of magnetic liquid and sound propagation in it*, Akust. Zh. **31**, 234–238 (in Russian)(1985).