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Ultrasonic Attenuation in Ferrofluids

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The absorption of acoustic energy by internal degrees of freedom of short chains is proposed as a new viable mechanism of ultrasound attenuation in ferrofluids. It is demonstrated that even though the volume fraction of the chains may be quite small, such an effect may reach the order of magnitude of viscous damping. In addition, by investigating the statistical properties of dimers in ferrofluids, it is shown that an applied magnetic field modifies the sound attenuation in a highly anisotropic manner. The proposed mechanism provides new insights into the fundamental issue of colloidal response, and in particular may lead to its utilization in novel experimental concepts.

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Ferrofluids, i.e. colloidal suspensions of ferromagnetic or superparamagnetic grains, display many unusual properties and fascinating phenomena [1-5]. Most of them – such as the surface instability in a constant magnetic field (so-called Rosensweig instability), labyrinthine structure in thin ferrofluid layers, magnetic birefringence under dc or ac fields, increase of the shear viscosity in a steady field and its decrease in a high-oscillating field – were predicted and/or explained in the model of *ideal* ferrofluid. The "ideality" means that magnetic grains interact with external magnetic fields but do not interact with each other. The latter limitation is justified if the *coupling constant* $\lambda = \mu^2/d_h^3 k_B T$ scaling the dipolar attraction of neighboring grains is sufficiently small, $\lambda \lesssim 1$; above $\mu = M_b V$ is the particle magnetic moment, M_b the bulk magnetization of particle material, and $V = \pi d^3/6$ is its magnetic volume: the hydrodynamic particle diameter d_h usually exceeds its magnetic diameter d.

Large λ values and perceptible volume fractions of the grains $\phi = nV$ (n is their number density) lead to formation of magnetic particle *chains* that is bringing together ferrofluids with magneto-rheological suspensions containing big ferromagnetic grains: their diameter is 2-3 orders larger than that in ferrofluids. This change in ferrofluid microstructure gives rise to such novel properties as elasticity or yield stress and significantly changes the ferrofluid viscosity. Those effects have been recently observed in real experiments [6-7] and studied analytically and numerically [8-9].

Detecting the particle association is a serious experimental problem. Indeed, one has to judge the chains using only indirect data on magnetoviscosity [6-11]. There exists, however, an experiment which is very sensitive to even weak deviations of ferrofluid features from ideality. We are talking about the sound absorption. Among some mechanisms of absorption acting in colloidal suspensions only two ones depend on external magnetic fields and then are magnetically controlled. One of the two is provided by the magnetization relaxation. This mechanism acts in ideal as well as in non-ideal ferrofluids: it does not require interparticle interactions. Actually, sound waves shift an equilibrium magnetization $\mathbf{M}_{\rm eq}$ in a steady magnetic field $\mathbf{H}$: Both the values get small additions, $\delta\mathbf{M}$ and $-4\pi\delta\mathbf{M}$, proportional to the fluid velocity $\mathbf{v} = \mathbf{v_0}\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)$. Relaxation of the magnetization $\mathbf{M}$ to the new equilibrium is accompanied with a dissipation of the sound wave energy. However, this mechanism of absorption has turned out to be ineffective (corresponding calculations will be published in other place).

The second mechanism of sound damping in magnetized ferrofluids is attributed to an internal chain dynamics [12,13]. Taketomi [12] has assumed existence of infinitely long chains lined up in the field direction. His chains are composed out of spherical *clusters* of diameter $\sim 1\,\mu$m, each of the clusters contains $\sim 10^5$ (!) "elementary" magnetic grains of $d \sim 10\,$nm. Later, Pleiner and Brand [13] have proposed a similar but somewhat more realistic model. They also consider the chains in a strong magnetic field, but their chains are formed out of grains – not of the clusters! According to Ref. [14], "it is necessary that the [sound] wavelength is comparable with the chain length". To satisfy this condition at the sound frequency $\omega/2\pi = 3\,$MHz the chain has to be longer than $0.5\,$mm , i.e. it contains $N \gtrsim 25,000$ magnetic grains. The mean number of particles in a chain $\langle N\rangle$ strongly depends on λ (it stands in exponent) and weakly on the dimensionless field strength $\xi = \mu H/k_B T$ and the particle concentration ϕ (see [14,15]). In the limiting case

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TABLE I: Distribution of magnetic grains upon oligomers

ξ	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	$\sum_{i=1}^{4}\phi_i$	$\langle N\rangle$
0	6.71	2.43	0.66	0.16	0.04	10.00	1.22
∞	5.40	2.86	1.14	0.40	0.13	9.93	1.36

$\xi \gg 1$ and $\phi = 5\,\%$ the value $\langle N\rangle = 25,000$ is reached for $\lambda = 15$. It is too much (λ stands in exponent of the chain partition function!). Ferrofluids with magnetite particles of $d = 14\,\mathrm{nm}$ and $d_h = 18\,\mathrm{nm}$ have $\lambda = 2$, while in commonly used commercial fluids the grains are smaller ($d \simeq 10\,\mathrm{nm}$) so λ for them is about unity.

Let us consider the case $\lambda = 2$ and $\phi = 10\,\%$ as an example of ferrofluid weakly deviating from ideality. Such a fluid does not contain long chains [16] but only single particles (monomers) and lowest *oligomers*: dimers, trimers, and so on. The distribution of magnetic grains upon these small clusters is presented in the Table 1 where the volume fraction of N-mers in a colloidal solution is defined as $\phi_N = N n_N V$ and n_N is the number density of N-mers. As seen from the Table, solitary grains constitute the majority, while the number of penta- and highest oligomers is negligible. Magnetic field slightly shifts the distribution to the side of higher oligomers: mean number of grains in the "chain" increases from 1.22 to 1.36.

Above we mentioned that the contribution of solitary grains to the sound absorption can be ignored. As for dimers, their number is rather small. Nevertheless as shown below it is enough to provide sound damping comparable with the viscous one.

We start the study of sound wave attenuation by examining the excitation of dimers oscillations by the fluctuating acoustic flow field. The dimers are modelled as pairs of equal-mass grains that are bound to each other due to the potential provided by magnetic dipole attraction and entropic and steric repulsion

$$U = \frac{1}{2} C\big(r - \langle r\rangle\big)^2, \qquad (1)$$

where r and $\langle r\rangle$ are the instantaneous, and the mean equilibrium distance between the particles in each dimer, respectively. The former can be expressed as $r = |\mathbf{r}_1(t) - \mathbf{r}_2(t)|$ where $\mathbf{r}_{1,2}(t)$ describe the time dependent particle location. The value of the dimer's elastic constant may be obtained from the law of equipartition, $\langle U\rangle = k_B T/2$, and is given by

$$C = \frac{k_B T}{\langle r^2\rangle - \langle r\rangle^2}\,. \qquad (2)$$

The field-dependence of C for two magnitudes of λ is shown in Fig. 1.

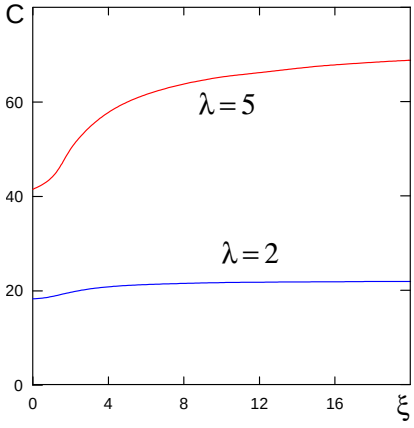

FIG. 1: The elastic constant as a functions of external field for two values of λ.

The equations of motion of the two particles in each dimer are given by:

$$m\ddot{\mathbf{r}}_1 + \gamma\dot{\mathbf{r}}_1 + \frac{\partial U}{\partial \mathbf{r}_1} = \gamma \mathbf{v}_0 \cos(\mathbf{k}\cdot\mathbf{r}_1 - \omega t)\,, \qquad (3)$$

$$m\ddot{\mathbf{r}}_2 + \gamma\dot{\mathbf{r}}_2 + \frac{\partial U}{\partial \mathbf{r}_2} = \gamma \mathbf{v}_0 \cos(\mathbf{k}\cdot\mathbf{r}_2 - \omega t)\,, \qquad (4)$$

where $\gamma = 3\pi\eta d_h$ is the Stokes drag coefficient, and η is the fluid's viscosity. The low dimer's concentration allows us to neglect an interaction between them.

It is convenient to introduce the center of mass vector of the dimer $\mathbf{r}_c$ and the distant (center-to-center of the grains) vector $\mathbf{r}$:

$$2\,\mathbf{r}_c = \mathbf{r}_1 + \mathbf{r}_2\,, \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2\,. \qquad (5)$$

Adding and subtracting Eqs. (3) and (4) and taking into account that $\langle r\rangle$ is much less than the sound wavelength, $(\mathbf{k}\cdot\mathbf{r}) \ll 1$, we arrive at the following equations:

$$m\ddot{\mathbf{r}}_c + \gamma\dot{\mathbf{r}}_c = \gamma \mathbf{v}_0 \cos\omega t\,, \qquad (6)$$

$$m\ddot{\mathbf{r}} + \gamma\dot{\mathbf{r}} + 2\,\frac{\partial U}{\partial \mathbf{r}} = \gamma \mathbf{v}_0 (\mathbf{k}\cdot\mathbf{r}) \sin\omega t\,. \qquad (7)$$

The first of them describes the motion of a dimer as a whole, while the second governs the internal vibrations along the dimer's axis. The ratio $\gamma/m = 18\eta/\rho_p d^2$ (here ρ_p is the particle density) determines some characteristic frequency which for $d \sim 10\,\mathrm{nm}$ is of the order of $10^{11}\,\mathrm{s}^{-1}$. Therefore, being interested in ultrasound frequency less than 10 MHz, one can easily neglect the inertia terms in Eqs. (6) and (7). Linearizing now Eq. (7) about the mean equilibrium distance, $r = \langle r\rangle + \varepsilon(t)$, and substituting $\mathbf{v}_0 = v_0\mathbf{k}/k$ we arrive at the equation for an average dimer's deformation

$$\dot{\varepsilon} + \varepsilon/\tau = v_0 k \langle r\rangle \langle \cos^2\alpha\rangle \sin\omega t\,, \qquad (8)$$

that depends on the angle α between the wave vector $\mathbf{k}$ and the dimer's axis $\mathbf{r}$: the fluctuating acoustic flow

excites the maximal amplitude of dimer oscillation when $\mathbf{k}\|\mathbf{r}$ ($\alpha = 0$), while in the opposite geometry, $\mathbf{k}\perp\mathbf{r}$ ($\alpha = \pi/2$) no compression or dilution within the dimer occur. We have introduced in Eq. (8) the relaxation time of dimer oscillations

$$\tau = \frac{\gamma}{2C} = 3\tau_B \frac{\langle r^2\rangle - \langle r\rangle^2}{d^2}\,, \qquad \tau_B = \frac{3\eta V}{k_B T}\,; \tag{9}$$

as seen, τ is scaled by the Brownian diffusion time τ_B for a single particle. The solution of Eq. (8) reads

$$\varepsilon(t) = \frac{v_0}{c}\langle r\rangle \frac{\omega\tau}{\sqrt{1+\omega^2\tau^2}}\langle\cos^2\alpha\rangle \sin(\omega t - \beta)\,, \tag{10}$$

where $\beta = \arctan\omega\tau$. The energy dissipation rate $D = n_2\gamma\overline{\dot\varepsilon^2}$ and the sound damping coefficient $\kappa_d = D/\rho c v_0^2$ are expressed through the solution (10):

$$\kappa_d = \frac{9\eta\phi_2}{2\rho c^3}\,\langle\bar r\rangle^2 \frac{\omega^4\tau^2}{1+\omega^2\tau^2}\,\langle\cos^2\alpha\rangle^2. \tag{11}$$

Here $\phi_2 = 2n_2V$ is the volume fraction of dimers, n_2 is their number density, and $\langle\bar r\rangle = \langle r\rangle/d$.

Let us compare the effect of the dimers on the sound attenuation (11) to the viscous absorption coefficient $\kappa_\eta = 2\eta\omega^2/3\rho c^3$. The relative attenuation is given by:

$$R \equiv \frac{\kappa_d}{\kappa_\eta} = \frac{27\phi_2}{4}\,\langle\bar r\rangle^2 \frac{\omega^2\tau^2}{1+\omega^2\tau^2}\,\langle\cos^2\alpha\rangle^2. \tag{12}$$

Almost all magnetic field dependence of R is hidden in $\langle\cos^2\alpha\rangle^2$ (indeed, ϕ_2, $\langle\bar r\rangle$ and τ weakly depend on the field strength ξ). In the absence of field the dimer's orientation is random and consequently $\langle\cos^2\alpha\rangle = 1/3$ (due to double-directedness of the distant vector $\mathbf{r}$ its orientation is described by the symmetric tensor $r_i r_k$ that just leads to the squared cosine). Applied magnetic field induces *uniaxial anisotropy* as the dimers tend to align along it. The degree of this anisotropy is given by the function

$$S(\lambda,\xi) = \frac{3}{2}\Big(\langle\cos^2\theta\rangle - \frac{1}{3}\Big)\,, \tag{13}$$

where θ is the angle between $\mathbf{r}$ and the applied magnetic field $\mathbf{H}$. This function is depicted in Fig. 2. Note that the saturation value of S at $\xi\to\infty$ depends on λ. Indeed, even the perfect orientation of particle magnetic moments $\boldsymbol{\mu}_2$ and $\boldsymbol{\mu}_2$ along a strong magnetic field does not influence the direction of $\mathbf{r}$ if $\lambda \ll 1$. So, $S(2,\infty) = 0.560$, $S(5,\infty) = 0.728$, and only $S(\infty,\infty) = 1$.

Estimations of $S(\lambda,\xi)$ and the other average quantities needed to calculate the relative absorption coefficient R are obtained from the statistical properties of the dimers in the presence of an applied magnetic field. The latter has been studied extensively in [] and [] where the dimers' partition function has been calculated and investigated.

The discussing problem contains two fixed vectors, $\mathbf{k}$ and $\mathbf{H}$, and hence only one fixed angle φ between them. Simple geometrical considerations reveal that

$$\langle\cos^2\alpha\rangle = \frac{1}{3}\big(1-S\big) + S\cos^2\varphi\,. \tag{14}$$

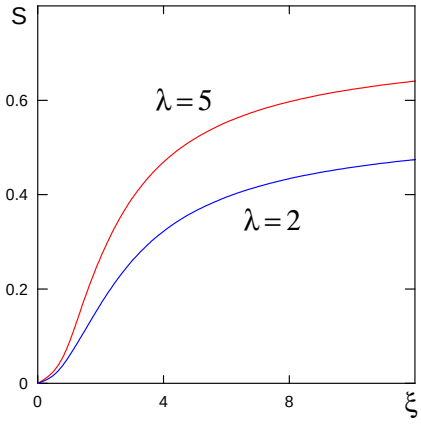

FIG. 2: Order parameter S as a functions of external field for two values of λ.

Thus, the field-induced anisotropy S may change dramatically the value of $\langle\cos^2\alpha\rangle^2$ and consequently that of R. This relative absorption coefficient can be written as

$$R = \frac{3\phi_2\langle\bar r\rangle^2}{4}\,\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\,f(\varphi)\,, \tag{15}$$

$$f(\varphi) = [(1-S) + 3S\cos^2\varphi]^2\,, \tag{16}$$

where the function (16) reveals strong anisotropy: it takes the magnitude $(1+2S)^2$ if the sound wave propagates along the field, $\varphi = 0$, and $(1-S)^2$ in the opposite geometry, $\varphi = \pi/2$.

Let us estimate the effect of the dimers on ultrasound absorption in the magnetite ferrofluid whose composition is presented in Table 1. For $\xi = 12$ that corresponds to $H \simeq 700$ Oe and $\lambda = 2$ one obtains $S = 0.480$, $\langle\bar r\rangle = 1.17$, and $\phi_2 = 2.8\%$. Taking into account the difference between the magnetic and hydrodynamic particle's diameters and assuming the ferrofluid viscosity $\eta = 10$ cP we find $\tau_B = 2.3\times10^{-5}$ s and $\tau = 3.2\times10^{-6}$ s (see Eq. (9)). Then for the sound frequency $\omega/2\pi = 3$ MHz the product $\omega\tau$ reaches 60 so the frequency-dependent factor in Eq. (15) transforms into unity. Substituting the above values in Eqs. (15)-(16) gives the relative absorption coefficient R as a function of φ. At $\varphi = 0°$ it reaches its maximal value which is 23.5% of the viscous damping coefficient.

Further ultrasound attenuation occurs due to the effect of higher N-particle oligomers, with $N \geq 3$. Under the conditions specified above (namely, relatively low value of λ), the oligomers may be considered as short flexible chains with $q = 3N - 6$ oscillatory degrees of freedom, each of which absorbs ultrasound as a single dimer. Consequently, considering – in addition to dimers – only tri-, tetra- and pentamers, the number density of *effective* absorbing *dimers* is given by $n_2^{\rm eff} = n_2 + 3n_3 + 6n_4 + 9n_5$.

Then the effective volume fraction of the dimers is

$$\phi_2^{\rm eff} = 2Vn_2^{\rm eff} = \phi_2 + 2\sum_{N=3}^{5} \frac{3N-6}{N}\,\phi_N\,, \qquad (17)$$

where ϕ_N is the volume fraction of N-particle oligomers. Replacing ϕ_2 in Eq. (15) by $\phi_2^{\rm eff}$ from (17) reveals that the effective absorption coefficient for the ϕ_N-distribution presented in Table 1 is given by $R_{\rm eff} = 2.38R$. Thus, when the magnetic field of the dimensionless strength $\xi = 12$ is aligned with the direction of sound propagation, the absorption coefficient due to vibrations of oligomers is as high as 56% of the viscous damping coefficient. The angular dependence of $R_{\rm eff}$ is presented in Fig. 3 for three magnitudes of the magnetic field strength. The anisotropy of the sound damping is very similar to that experimentally observed recently in Ref. [17].

To summarize, it has been shown that even small deviation of ferrofluids from ideality gives rise to a significant sound damping. This is in contrast to the magnetization relaxation mechanism which is ineffective in sound attenuation. The non-ideal sound absorption originates from the internal dynamics of chains of various lengths that are invariably formed in ferrofluids, and has been shown to strongly depend on the externally applied magnetic field.

Commonly used ferrofluids are characterized by the coupling constant of the order of unity and hence contain mainly single grains and a small portion of chains of a few links like dimers, trimers, and tetramers. The main mechanism responsible for the sound attenuation is the absorption of the energy of the fluctuating acoustic flow field by the oscillatory degrees of freedom of the short chains. Each of the degrees of freedom acts as an effective dimer in attenuating sound.

The absorption coefficient due to that process has been calculated and was shown to constitute a significant portion of the viscous damping for the most popular magnetite ferrofluids. In particular, it has been shown that the applied magnetic field induces in such ferrofluids a high enough uniaxial anisotropy. Thus, for a 3 MHz ultrasound that propagates perpendicular to an applied magnetic field of strength $\xi = 12$ the additional attenuation due to the total number of effective dimers is only 4% of that of viscous damping. However, if the same magnetic field is aligned with the direction of the ultrasound propagation, its effect dramatically increases and reaches up to 56% of the viscous sound attenuation.

It is envisioned that such a remarkable anisotropy may be employed in a variety of laboratory applications. One such obvious application is the direct measurement of the average orientation of grains in ferrofluids. The latter, represented by $S(\lambda, \xi)$, can be inferred from measurements of attenuation of sound waves that propagate parallel and perpendicular to the applied magnetic field.

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