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The influence of the concentration of ferroparticles in a ferrofluid on its magnetic and acoustic properties

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Abstract
This paper reports results of a study of magnetic and acoustic properties of a ferrofluid, EMG-605. The measurements were performed for three samples of the same ferrofluid differing in concentration. The magnetic susceptibility was measured as a function of an external magnetic field for each sample, which allowed us to determine the magnetization curves and saturation magnetization. The results provide information on the mean magnetic moment and the mean radius of the magnetite grain. In the samples subjected to an external magnetic field, the anisotropy of the ultrasonic wave absorption coefficient was determined. The mechanisms of ultrasonic wave energy dissipation through the translational and rotational degrees of freedom were established for some ferrofluid concentrations.

1. Introduction

Ferrofluids are colloidal suspensions of single-domain magnetic nanoparticles in a carrier liquid medium. The magnetic particles are coated with a molecular layer of a dispersant compatible with both the carrier liquid and the magnetic particles. Ferrofluids are usually described as magnetically soft materials, because the magnetization vector follows the applied field without hysteresis. Owing to their exceptional physical properties, ferrofluids have recently found wide application in technology [1] and medicine [2]. Their use in loudspeakers, in rotating elements of machines for sealing rotating rollers or in devices absorbing vibrations (as a means of electrically controlled elasticity) is well known. In medicine, ferrofluids are used to *in vivo* target drugs by selective adsorption of medicines on the coating of the magnetic particles, which can be enriched subsequently in a specific tissue of the body by applying external magnetic fields.

Ultrasound propagation in a magnetic fluid under an external magnetic field was studied by several authors both theoretically and experimentally. Parsons [3] proposed a linear hydrodynamical theory of a magnetic liquid assuming the magnetic fluid to be a nematic liquid crystal. His theory predicted the dependence of the ultrasound attenuation and velocity on the angle, θ, between the sound wave vector and the external magnetic field. The existence of such anisotropic behaviour was later confirmed experimentally [4, 5], but the exact dependence of the velocity and attenuation on the angle appeared to be different from the $\sin^2 2\theta$ predicted in Parsons' theory. A promising model that offered a description of the characteristic features of attenuation of ultrasound waves in magnetic liquids was given by Taketomi [6]. His model takes into account the rotational and translational motions of magnetic particle clusters or cluster chains and it seems to be able to explain, at least qualitatively, experimental findings [7]. Despite other efforts [8, 9] Taketomi's theory remains the most useful in describing sound attenuation anisotropy in ferrofluids.

An externally applied magnetic field induces ordering of the magnetic moments of the particles, giving rise to magnetization of the sample as a whole on a macroscopic scale. In dilute ferrocolloids the energy of interparticle dipole–dipole interactions is small compared with the heat energy. Under the effect of an external magnetic field the ferrofluid structure is rearranged. When the concentration of the solid component is sufficiently high and the intensity of the magnetic field is strong enough to stimulate formation of chain clusters, the rigidity of the ferrofluid increases, which affects the conditions of ultrasonic wave propagation in this medium. The structural changes are also manifested by a considerable dependence of the ultrasonic wave absorption on the magnetic field intensity for different concentrations of ferroparticles in the ferrofluid. An external magnetic field induces an anisotropy of the parameters describing both propagation of ultrasonic waves in the ferrofluid and magnetic susceptibility. In this paper, we will report the results of our experimental studies of magnetic properties and the ultrasonic anisotropy of a ferrofluid and compare the experimental findings with the existing theories. At equilibrium, the magnetization can be expressed as a superposition of the Langevin functions, revealing thus a natural polydispersedness of the particles [10]:

$$M_{\rm L} = \sum_i m_i n_i L(\xi_i), \qquad L(\xi) = \coth(\xi) - \frac{1}{\xi}, \tag{1}$$

where $\xi = \mu_0 m_i H/kT$, $\mu_0 = 4\pi \times 10^{-7}\,{\rm H\,m^{-1}}$, m_i, n_i are the magnetic moment and particle number density, respectively, of the ith fraction and H is the intensity of the magnetic field. For weak magnetic fields, equation (1) leads to the Curie law for the initial magnetic susceptibility [11]:

$$\chi_{\rm L} = \frac{\mu_0 \langle m^2 \rangle n}{3k_{\rm B}T}, \tag{2}$$

implying a linear dependence of the magnetic susceptibility on the bulk concentration of the solid component in the ferrofluid. In real ferrofluids these predictions are not exactly fulfilled because of the interparticle interactions. To detect these interactions and assess their strength, three samples of the ferrofluid differing in the bulk concentration of the solid component were subjected to magnetic and ultrasonic studies.

2. Experiment

The study was performed for three samples of ferrofluids containing different concentrations of magnetite: $\phi_1 = 3.57\%$, $\phi_2 = 1.785\%$ and $\phi_3 = 0.893\%$. The values of dynamic viscosity, density and volume concentration of the parent sample denoted as '1' were approximately 0.005 Pa s, $1166\,{\rm kg\,m^{-3}}$ and 3.57%, respectively. The parent sample contained magnetite particles (Fe_3O_4) in the form of a colloidal solution in water. Their surface was covered with a thin layer of oleic acid to limit cluster formation. The bulk concentrations of the solid phase in the subsequent samples obtained from the parent solution were diminished by half.

The anisotropy of the ultrasonic attenuation wave was measured using the Matec pulse–echo technique (figure 1). A radio frequency gated amplifier, model 755, and gating modulator, model 7700, were used to drive the piezoceramic transducer. The ultrasonic pulse, on traversal of the sample, was detected by the receiver transducer and amplified in a wide-band amplifier. The resulting pulse–echo train was observed on a CRT display. The model 2470 B automatic attenuation recorder measures the logarithmic difference (in dB) between two selected echoes, say A and B, if the time gates correctly cover the main portion of the echoes. When A and B are two consecutive echos, the log(A/B) output is proportional to the absorption coefficient of the sample. The variations of log(A/B), e.g. as a function of the angle θ, give direct changes in the absorption coefficient. The absolute value of the ultrasound wave absorption was measured to an accuracy of ±3%. The frequency of the ultrasonic wave was 3.4 MHz. The ferrofluid studied was placed in a thermostated closed measuring cell with two piezoelectric transducers at a constant distance (1.54 cm). The cell contained 5 ml of the ferrofluid. The temperature of the ferrofluid was 25°C. For the angular dependence experiment the magnetic field was rotated by 5° each time, while the measuring cell remained stationary in the gap between electromagnetic pole pieces. The magnetic field induction was measured to within 0.5% with an F.W. Bell Gaussmeter, model 9200.

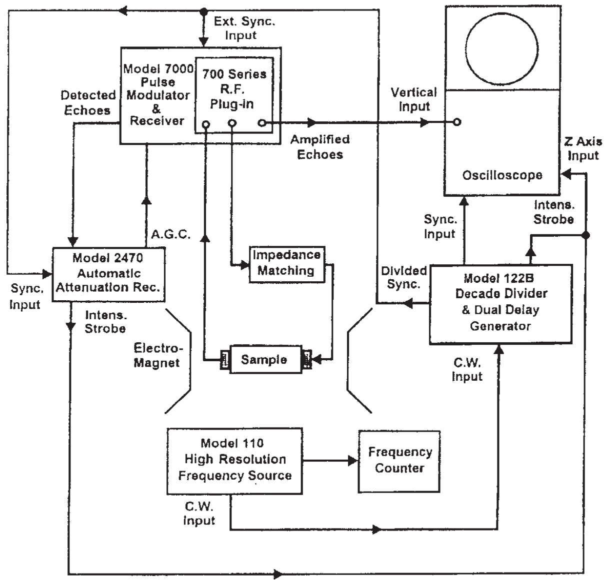

Figure 1. Block diagram of the experimental set-up.

3. Magnetic properties of the ferrofluid

Usually in a ferrofluid there are two mechanisms of magnetization: the Brown and Néel ones in force. According to the Brown mechanism [11] the magnetic moment is rotated together with the nanoparticle in the carrier liquid under the influence of an external magnetic field H. The time of magnetization relaxation according to this mechanism depends on the hydrodynamic volume, V, temperature, T, and dynamic viscosity, η, of the carrier liquid and can be expressed as

$$\tau_{\rm B} = \frac{3V\eta}{k_{\rm B}T}, \tag{3}$$

where the hydrodynamic volume of a particle V is much greater than the magnetic core. The Brown mechanism of magnetization of superparamagnetic particles can be blocked by decreasing the temperature of the ferrofluid till the carrier liquid is frozen, and then magnetization of ferrofluid can take place only according to the Néel mechanism.

According to the Néel mechanism [11] the magnetic moment can rotate inside a nanoparticle. An energy barrier must be overcome for this rotation to happen. The height of this barrier is equal to $K_1 v$, where K_1 is the magnetocrystalline anisotropy constant (for magnetite particles, $K_1 = 11\,{\rm kJ\,m^{-3}}$). The probability of getting over such a barrier is proportional to $\exp(K_1 v/k_{\rm B}T)$.

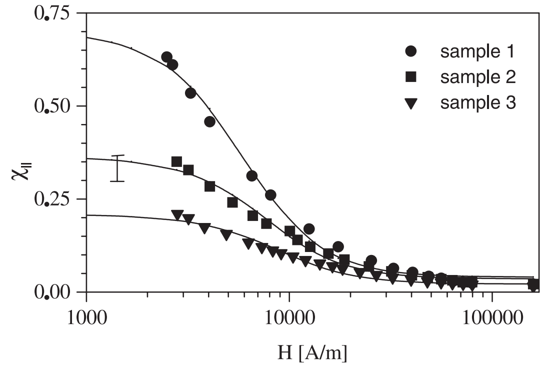

Figure 2. The magnetic susceptibility, $\chi_{\|}(H)$, for the parallel arrangement of the measuring cell axis to the direction of the constant magnetic field, H, for three samples of different ferrofluid concentrations: (1) $\phi_1 = 3.56\%$, (2) $\phi_2 = 1.785\%$ and (3) $\phi_3 = 0.893\%$ ($T = 293$ K, $f = 100$ Hz).

According to the Néel theory the relaxation time is

$$\tau_N = \tau_0 \exp\left(\frac{K_1 v}{k_B T}\right), \tag{4}$$

where $\tau_0 \simeq 1$ ns [2, 11].

In practice, in a ferrofluid the two mechanisms can take place simultaneously, and then the effective relaxation time of magnetization is

$$\tau_{\text{eff}} = \frac{\tau_B \tau_N}{\tau_B + \tau_N}. \tag{5}$$

As follows from equations (3) and (4), the mechanisms depend on the size of the nanoparticles. In a given ferrofluid the magnetization mechanism whose relaxation time is shorter dominates. In a polydispersive ferrofluid the Néel mechanism can dominate for some nanoparticles of size below a certain value, while for the others the Brown mechanism can be dominant.

In the range of low frequencies for which the magnetic susceptibility approaches its static value, the radius of nanoparticles can be measured by a method based on determination of the differential magnetic susceptibility.

If a ferrofluid studied is polarized by a constant magnetic field of intensity H, the differential magnetic susceptibility measured along this field is [11]

$$\chi_{\|}(\xi) = 3\chi_0 \frac{\mathrm{d}L(\xi)}{\mathrm{d}\xi} = 3\chi_0 \left[\frac{1}{\xi^2} - \frac{1}{\sinh^2 \xi}\right], \tag{6}$$

where $\xi = \mu_0 m_{\text{eff}} H / k_B T$.

The differential magnetic susceptibility of the ferrofluid, χ, was measured parallel ($\|$) to the direction of the constant magnetic field, H. The value of $\chi_{\|}$ was obtained by comparing the inductance of a measuring solenoid immersed in the medium studied with that of the same solenoid in the air. The inductance, L_1, of a cylindrical solenoid placed in the sample cell was indicated by the digital inductance meter to an accuracy of $\pm 0.25\%$. Figure 2 presents values of the differential magnetic susceptibility measured in the direction parallel to that of the constant magnetic field, H, and the functions $\chi_{\|}(H)$ obtained as a result of the fitting procedure.

Equation (6), describing the differential magnetic susceptibility, $\chi_{\|} = \mathrm{d}M_{\|}/\mathrm{d}H$, was used to represent the

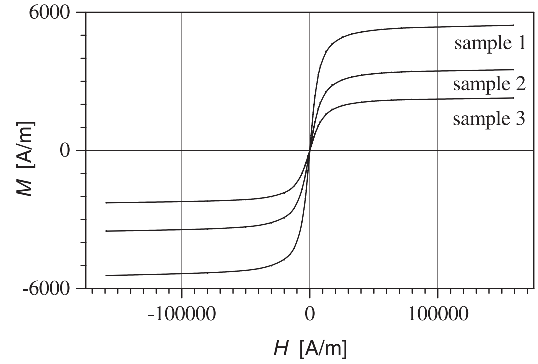

Figure 3. The magnetization, M, as a function of the constant magnetic field, H, for three samples with different ferrofluid concentrations: (1) $\phi_1 = 3.56\%$, (2) $\phi_2 = 1.785\%$ and (3) $\phi_3 = 0.893\%$.

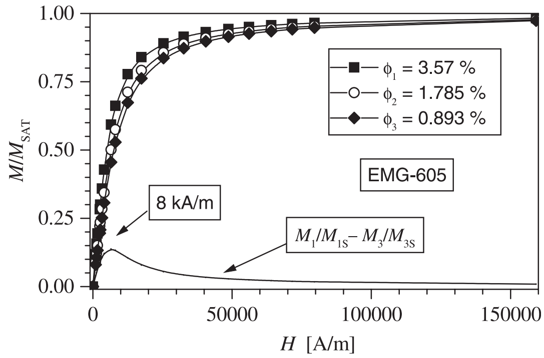

Figure 4. Normalized magnetization measured for the three ferrofluid samples studied.

magnetization, $M(H)$, of the ferrofluid in a constant magnetic field. Integration of $\mathrm{d}M_{\|}$ over the magnetic field intensity, H, gave the following expression:

$$M_{\|}(H) = \int_0^H \chi_{\|}\, \mathrm{d}H = M_{i\infty}\left[\coth\left(\frac{\mu_0 m H}{k_B T}\right) - \frac{k_B T}{\mu_0 m H}\right]. \tag{7}$$

In this expression, $M_{i\infty}$ stands for the magnetization of the ith sample in the state of saturation. The course of this dependence is shown in figure 3. For subsequent samples the following saturation values of magnetization were obtained: $M_{1\infty} = 5529$ A m^{-1}, $M_{2\infty} = 3591$ A m^{-1} and $M_{3\infty} = 2335$ A m^{-1}. The same procedure allowed determination of the moments of magnetic grains, which permitted an estimation of their size. In subsequent samples the radii of magnetic particles were determined as $r_1 = 8.3$ nm, $r_2 = 6.5$ nm and $r_3 = 4.1$ nm. The differences indicate the occurrence of interactions among the magnetic grains and the presence of magnetic clusters. The presence of interactions among the particles is also suggested by the normalized course of magnetization obtained for the three samples (shown in figure 4). For the zero magnetic field and for the state of saturation the curves coincide and the maximum deviation between them is noted for a field close to 8 kA m^{-1}.

4. Anisotropy of ultrasound wave absorption

Results of the magneto-optical experiments [11] on the ferrofluid samples subjected to an external magnetic field indicate a formation of chains arranged along the lines of the external field. The chains are composed of spherical clusters whose size can be estimated on the basis of Taketomi's theory [6]. Because of the polydispersivity of the magnetite particles forming the spherical clusters, the degree of packing is different. Moreover, coagulation of grains of greater size is easier. The energy of the propagating ultrasonic waves in a ferrofluid under the effect of an external magnetic field (so showing anisotropy of elastic and magnetic properties) is used for activation of the translational and rotational degrees of freedom. After Taketomi, the amplitude attenuation coefficient, $\alpha(\theta)$, of an ultrasonic wave in ferrofluids subjected to an external magnetic field consists of two parts, related, respectively, to the translational motion of the clusters, $\alpha_{\mathrm{tr}}(\theta)$, and their rotational motion, $\alpha_{\mathrm{rot}}(\theta)$:

$$\alpha_{\mathrm{tr}}(\theta) = \frac{1}{c}\frac{3\pi\eta_{\mathrm{S}} r_{\mathrm{cl}}\omega^3 V_{\mathrm{cl}} N(6\pi\eta_{\mathrm{S}} + V_{\mathrm{cl}}\omega\rho_0)}{(k^2\sin\theta - V_{\mathrm{cl}}\omega^2\rho_{\mathrm{m}})^2 + (6\pi r_{\mathrm{cl}}\omega\eta_{\mathrm{S}})^2}, \qquad (8)$$

$$\alpha_{\mathrm{rot}}(\theta) = \frac{\omega^2}{2\rho_0 c^3}\left(\frac{4}{3}\eta_{\mathrm{S}} + \eta_{\mathrm{V}} + 2\alpha_5\cos^2\theta + \alpha_1\cos^4\theta\right), \qquad (9)$$

where c is the velocity of the ultrasonic wave propagating with angular frequency ω, ρ_0 and ρ_{m} are the densities of the carrier liquid and magnetic particles, η_{S} and η_{V} are the dynamic and volume viscosities, r_{cl} and V_{cl} are the radius and volume of the cluster, N is the number of clusters per unit volume, k is the elastic force constant, θ is the angle between the magnetic field strength vector and the propagation vector of the ultrasonic wave and α_1, α_5 are the Leslie coefficients appearing in the theory of liquid crystals [12].

The clusters—under the influence of the sound wave—start to make translational and rotational motions simultaneously. This is an irreversible process leading to the dissipation of the energy of the acoustic wave. Figures 5–7 show the results of the anisotropy measurements, $\alpha(\theta)$, for a ferrofluid sample subjected to a constant magnetic field ($H_{\mathrm{DC}} = 159\,\mathrm{kA\,m^{-1}}$), fitted to the curves $\alpha(\theta)$ following from Taketomi's theory. Results of measurements of $\alpha(\theta)$ provide important information on the ferrofluid structure in a magnetic field. They are shown in table 1.

It should be noted that the sound velocity also contributes to the ultrasonic anisotropy in a magnetic liquid. However, the measurements carried out by the authors [14] in ferrofluid EMG-605 of concentration $\phi = 3.5\%$ showed the effect of velocity anisotropy to be quite small. It should be even smaller in a less concentrated ferrofluid. Moreover, there is no satisfactory theory that would allow us to draw conclusions about the structure of a ferrofluid on the basis of angular velocity measurements. Therefore our analysis of ultrasonic anisotropy in magnetic liquids is focused on attenuation.

Taking into account the concentrations of magnetite particles in particular samples and the results of the fit (N and r_{cl} from table 1), it is possible to estimate the percentage of magnetic particles involved in the chain clusters from the equation

$$q = \frac{N 4\pi r_{\mathrm{cl}}^3}{3V_{\mathrm{m}}} \times 100\%, \qquad (10)$$

where V_{m} is the total volume occupied by all magnetic particles (both bounded in the clusters and flowing freely in a carrier liquid). It is possible to estimate V_{m} from the concentration of the sample. The obtained per cent of magnetic particles forming the chain clusters in the samples was 8.5%, 18.3% and 12.5% for the concentrations $\phi_1 = 3.57\%$, $\phi_2 = 1.785\%$ and $\phi_3 = 0.893\%$, respectively. This means that despite a high intensity of the external magnetic field not all particles were engaged in cluster formation. It may seem strange that the per cent of the magnetic particles forming the chain clusters is higher for the ferrofluid of concentration 1.785% than of concentration 3.57%. This may be partly due to the way the samples were prepared. The sample with a lower concentration of magnetic particles was prepared by dilution of a more concentrated sample. Because the clusters are rather stable, the dilution mainly decreased the concentration of free magnetic

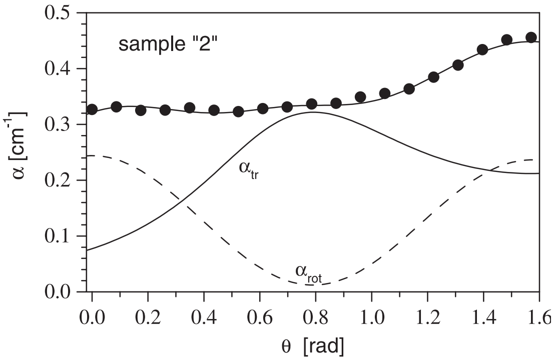

Figure 6. Anisotropy of ultrasonic wave propagation in the ferrofluid sample of concentration $\phi_2 = 1.785\%$.

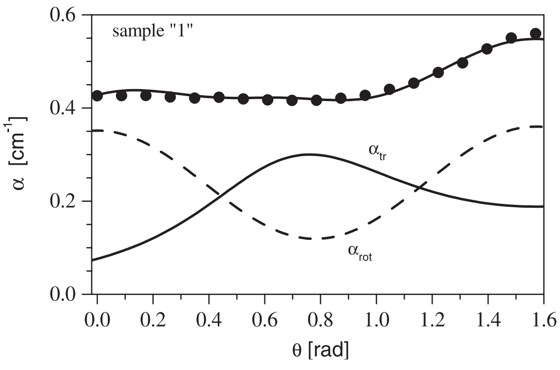

Figure 5. Anisotropy of ultrasonic wave propagation in the ferrofluid sample of concentration $\phi_1 = 3.57\%$.

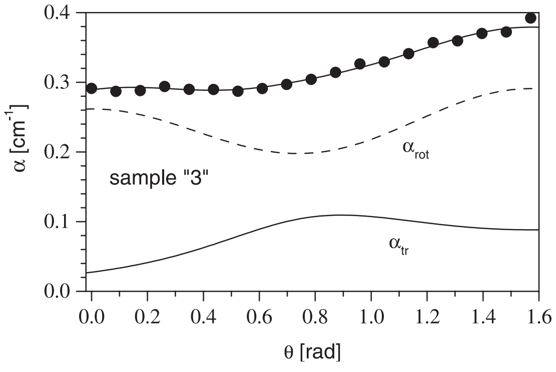

Figure 7. Anisotropy of ultrasonic wave propagation in the ferrofluid sample of concentration $\phi_3 = 0.893\%$.

Table 1. Values of the selected parameters $4\eta_S/3+\eta_V$, α_5, α_1, k, N and r_{cl} obtained from fitting the function describing the anisotropy of the ultrasonic absorption coefficient to the measured points ($T = 298$ K; $f = 3.4$ MHz, $H_{DC} = 159$ kA m^{-1}) using the least-square method.

Sample	$4\eta_S/3 + \eta_V$ (g cm^{-1} s^{-1})	α_5 (g cm^{-1} s^{-1})	α_1 (g cm^{-1} s^{-1})	k (dyn cm^{-1})	$10^{-8}N$ (cm^{-3})	r_{cl} (nm)
1	4.69	−6.22	12.33	305	341.47	277
2	3.08	−5.59	11.88	312	343.96	282
3	3.79	−2.22	4.06	273	122.0	278

particles in the carrier fluid, leading to the higher per cent of magnetic particles forming the chain clusters in the sample.

Experimental investigation of a ferrofluid by acoustic and magnetic methods provides valuable information on its structure and behaviour in an external magnetic field. It allows, among others, a determination of such parameters as mean radius of magnetic clusters, r_{cl}, and magnetic particles, r, and their magnetic moment, as well as the number of clusters per unit volume, N, and other quantities characterizing the ferrofluid. The methods described can be valuable tools for investigation of the anisotropy induced in a ferrofluid by an external magnetic field.

5. Conclusions

The magnetization of the ferrofluid samples measured in a state of saturation is not linearly dependent on the concentration of magnetite particles, which indicates the presence of interactions between the particles and formation of clusters. The presence of interactions between the magnetic particles is also suggested by the course of the normalized magnetization curves [13], which for the three samples show the greatest differences near $H_{DC} = 8$ kA m^{-1}. No hysteresis loop was observed in the magnetization dependence on the intensity of the external field for any of the samples. On the basis of the anisotropy of propagation of the ultrasonic waves the main parameters describing the structure of a ferrofluid subjected to an external magnetic field were determined including $4\eta_S/3 + \eta_V$, α_5, α_1, k, N and r_{cl}. The samples of higher concentration of magnetic particles are characterized by greater coefficients of dynamic and volume viscosity. On the other hand the radii of the spherical clusters apparently do not depend on the concentration. Although the anisotropy of the absorption coefficient of ultrasonic waves in ferrofluids was determined in a magnetic field causing magnetic saturation of the medium, still not all magnetic particles were involved in formation of clusters. The majority of the particles were free in the carrier fluid. The component $\alpha_{tr}(\theta)$ of the absorption coefficient of the ultrasonic waves, describing the loss of energy for activation of translational degrees of freedom of the clusters reaches a maximum at $\theta = \pi/4$ rad, at which the other component, $a_{rot}(\theta)$, reaches a minimum.

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