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Thermal Conductivity Measurements of the $CoFe_2O_4$ and γ-Fe_2O_3 based Nanoparticle Ferrofluids*

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Magnetic nanoparticles $CoFe_2O_4$ and γ-Fe_2O_3 ($8–15 \times 10^{-9}$ m) were dispersed in liquid carriers water and n-decane. Thermal conductivities of thus produced ferrofluids were measured at 25 °C in a magnetic field and they decreased with increasing the field strength up to $2–3 \times 10^{-2}$ T, which was followed by field independence in higher fields. The importance of the field dependent thermal conductivity of ferrofluids is discussed in terms of suitability of their application in loudspeakers.

INTRODUCTION

Thermal conductivity of ferrofluids and other nanofluids is their frequently quoted physical property in scientific literature.[1,2] Even comparatively small concentrations of nanoparticles in the carrier liquid considerably enhance their thermal conductivity, and in addition to theoretical interest in this topic, practical importance of the phenomenon resides on heat removal from parts of electrical machines. Excess heat released in the vibrating voice coil of an electrodynamic loudspeaker is commonly removed by highly heat conducting ferrofluids[3] being suspended and self supported in the air gap of the permanent magnet. Application of ferrofluids in loudspeakers results in suppression of short-term power handling in these devices.[3]

On the other hand, magnetic particles of a nanometer size are attracting increasing interest in the fundamental and technological area because of their unique magnetic properties, which are dominated by superparamagnetism, that is, magnetization curve exhibits no hysteresis. The unique properties of nanoparticles and the size dependence of those properties have led to a number of technological and biomedical applications of these materials, including the production of ferrofluids.

Magnetic fluids or ferrofluids are stable colloidal dispersions of monodispersed, single domain nanoparticles of ferro- or ferrimagnetic materials in a carrier liquid. Ferrofluid stability requirements depend: first, on the dimension of the nanoparticles, sufficiently small to avoid sedimentation due to gravitation, and second, on the surface-surface repulsion, provided by steric and/or coulomb interactions, which prevent agglomeration due to the Van der Waals and magnetic dipole forces. In this respect, nanoparticles can either be coated by a dispersant (Fig-

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

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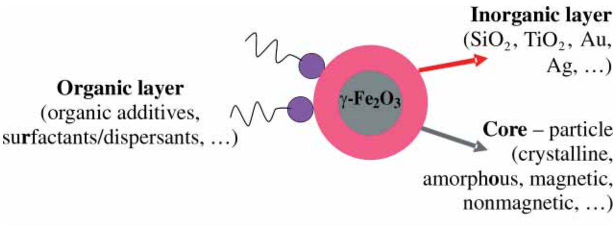

Figure 1. A magnetic nanoparticle and layer of organic molecules.

ure 1), which gives rise to entropic repulsion between them, or the surface of the particle can be charged, thereby producing electrostatic or coulomb repulsion.

A variety of carboxylic acids represent a group of dispersive agents that have been most often used for steric stabilization of nanoparticles in a liquid medium. The carrier liquid is selected to meet the particular application requirements and can be a hydrocarbon, ester, perflouropolyether, water, *etc*. According to the type of carrier liquid, two types of ferrofluids are distinguished: aqueous ionic and surfacted organic-based ferrofluids. Ionic ferrofluids demonstrate several specific phenomena; in particular, they may be used as precursors to a wide class of surfacted ferrofluids, based upon low-evaporating non-polar liquids, keeping their fluid properties in a rather wide temperature range.

High specific magnetization of ferrofluids and their long-term stability have made them useful in a wide range of applications such as sealing, dumping, cooling, bearing, sensing devices, *etc*. In biomedicine, they are used for diagnostic and therapeutic applications (MR imaging, targeting drug delivery, hyperthermia, magnetic cell separation).

Although attractive magnetic properties and their applications in loudspeakers suggest measurement of thermal conductivity in a magnetic field, no report on the subject has been found in the literature to date. In this paper, measurements of thermal conductivity in a magnetic field were performed and the results were interpreted in terms of the existing models of superparamagnetic materials.[4]

EXPERIMENTAL

Evaluation of a conventional ferrofluid involves at least three fundamental requirements: first, synthesis of nanoparticles with a narrow particle size of around 10^{-8} m must be proved; second, surface treatment of nanoparticles is required in order to prevent them from agglomeration, and third, peptization of nanoparticles into the carrier liquid must be performed, required for the stability of the magnetic fluid.

In the first step, monodispersed particles of superparamegnetic maghemite (γ-Fe_2O_3) and of cobalt ferrite ($CoFe_2O_4$) were prepared using the classical coprecipitation method. The monoparticle synthesis was carried out by alkalizing a 1:2 mixture of M^{II} (M = Co, Fe) and Fe^{III} at elevated temperature under vigorous stirring, and by the use of commercially available reagents. In this method, the corresponding metal hydroxides were precipitated during the reaction between the precipitating reagent and an aqueous solution of the metal salts. The metal hydroxides were subsequently oxidized in air, which was indicated by formation of the spinel phase.

Variation of the reaction parameters (pH, reaction temperature, reaction time, mixing velocity and concentration of reactants) provided nanoparticles with a mean size ranging from 8 to 15×10^{-9} m and relatively high specific magnetizations of around 60 emu/g.

In order to prevent mutual sticking of nanoparticles, as well as subsequent agglomeration, the particles were sterically stabilized by absorption of a thin layer of oleic acid or ethylene glycol as dispersive agents onto their surface, followed by electrostatic stabilization by controlling the pH and ionic strength of acidic or alkaline aqueous solutions.

Surface modified nanoparticles were finally dispersed in water and n-decane as carrier liquids in order to obtain high quality aqueous and organic-based ferrofluids of long-term stability (Figure 2). When put in a magnetic field, fer-

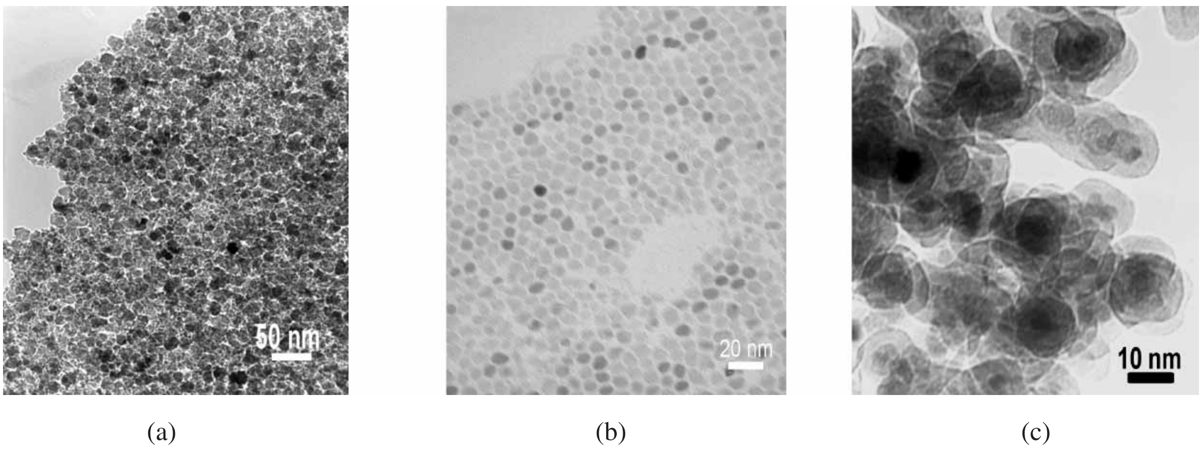

Figure 2. (a) Dry powder of magnetic nanoparticles, (b) magnetic nanoparticles coated with organic layer, (c) magnetic nanoparticles coated with inorganic layer.

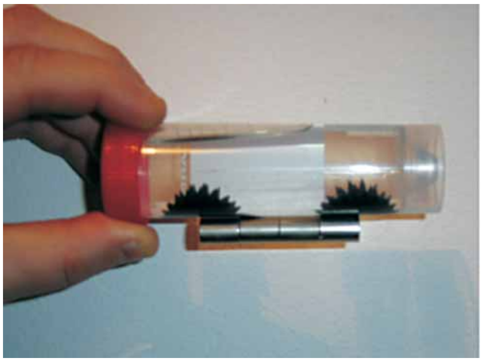

Figure 3. Magnetic liquid based on water as carrier in a permanent magnet field.

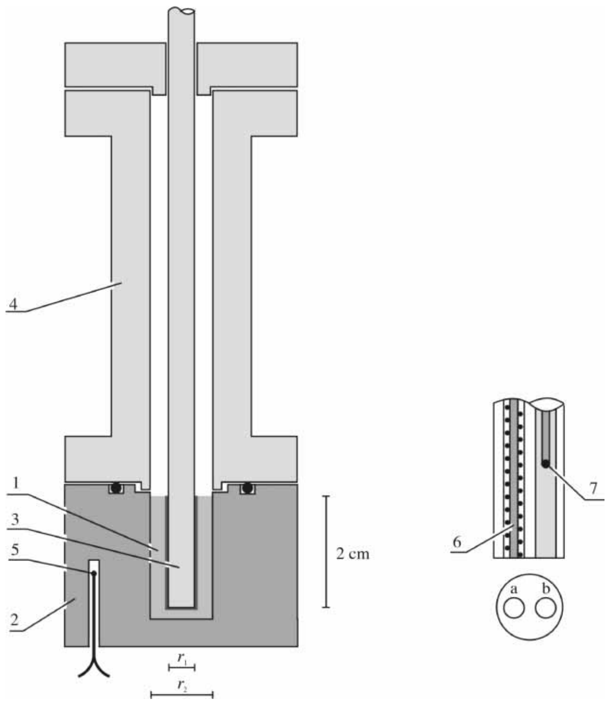

Figure 4. Thermal conductivity measuring device.

rofluids tend to conform to magnetic lines near S and N poles of the nearby permanent magnet (Figure 3).

Thermal conductivity was measured by the radial heat flux method applied in the measurement of high pressure dependent thermal conductivity of isopentane[5] used as isostatic pressure transmitting medium in high pressure (12 kbar) cells, and the measuring device (Figure 4) contained the sample of liquid (1) embedded in a copper can (2) serving as a heat sink, with inner hole diameter r_2 = 6 mm. Alumina stud (3) of diameter r_1 = 3 mm with two parallel axial holes served as a heat radiator of heating length l = 20 mm. The heater (6) consisted (Figure 4) of a 50 μm silk insulated manganin wire wrapped around a 0.4 mm copper wire for better thermal homogeneity. Copper-constantan thermocouple (7) was sealed in a thin indium wire and positioned in the nearby hole. Aluminum frame (4) ensured good centering of the alumina stud. The other end of the differential thermocouple was embedded in the copper heat sink (5), and in order to increase the uniformity of heat release, the active part of the alumina stud was enclosed by 20 μm silver foil. The driving current I = 20–50 mA to the heater (R = 16 ohm) oscillating at 5×10^{-3} Hz frequency was supplied from a SR 730 lock-in amplifier and thermocouple output ΔT oscillating at double frequency was detected at the amplifier A-B input.

Thermal conductivity is given by the expression:

$$\lambda = \frac{I^2 R}{2\pi \cdot \Delta T \cdot l} \cdot \ln\left(\frac{r_2}{r_1}\right) \tag{1}$$

Longitudinal heat losses in the alumina stud were estimated by an operation of the calorimeter in air and were nearly 4 percent of the lateral heat flux, which should be subtracted from the driving heat power. A similar correction of heat losses was done at the bottom of the alumina stud when the liquid was filled up to the bottom, and losses were evaluated by the above cited ac heating run. In order to check the possible influence of the magnetic field on the thermocouple sensitivity, a blank experiment was performed with distilled water and thermal conductivity was found to be 0.635 W m^{-1} K^{-1} at 25 °C, which is in satisfactory agreement with the value 0.610 W m^{-1} K^{-1} reported in the literature.[6] The magnetic field was generated by an external coil receiving current from DC power supply with about 0.5 percent stability.

Magnetic field dependences (Figure 5) of thermal conductivities of four ferrofluid samples indicate a decrease with increasing the field for low fields, and a rather constant value for higher fields. The strongest relative decrease of thermal conductivity with the magnetic field was observed in $CoFe_2O_4$ nanoparticles (sample 1) with specific magnetization 65 emu/g, dispersed in water (≈ 150 g/L). Sample 2 is γ-Fe_2O_3, with specific magnetization 55 emu/g, dispersed in water (≈ 120 g/L). Nearly independent of the field (sample 4) was thermal conductivity of γ-Fe_2O_3 dispersed in water (≈ 65 g/L). Sample 3 is γ–Fe_2O_3 dispersed in n-decane (≈ 300 g/L).

DISCUSSION AND CONCLUSIONS

The attempt[7] to interpret the enhancement of thermal conductivity in nanofluids by the Maxwell model of electrical conductivity[8] in heterogeneous media failed in two aspects. Firstly, the strength of enhancement by increasing the concentration of nanoparticles in the carrier fluid is much higher than predicted by the Maxwellian approach. Secondly, this approach predicts the $T^{1/2}$ temperature dependence of thermal conductivity, which contradicts the measurements data giving linear dependence.[2] In addition, the magnetic field dependence reported in this paper cannot be explained by this model either.

Evidently, the particle motion and mass transport (convection) must be taken into account, which has been done in the work of Kumar and co-workers.[9] Nanoparticles in the fluid behave according to the rules of the Brownian motion, and the Stokes-Einstein diffusion is the

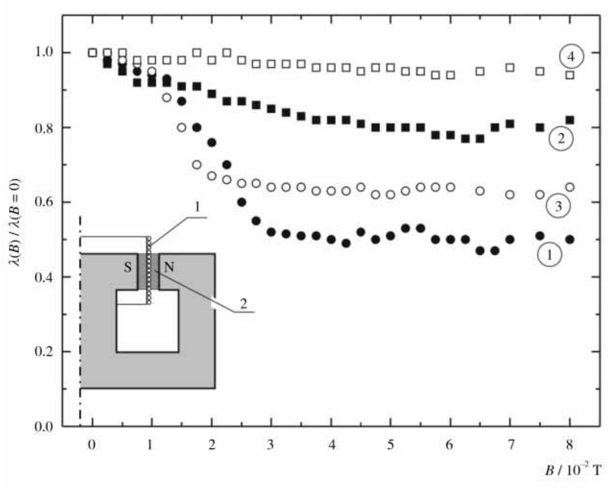

Figure 5. Magnetic field dependence of thermal conductivities of: (1) $CoFe_2O_4$ dispersed in water (≈ 150 g/L), (2) γ-Fe_2O_3 dispersed in water (≈ 120 g/ L), (3) γ-Fe_2O_3 dispersed in n-decane (≈ 300 g/ L), (4) γ-Fe_2O_3 dispersed in water (≈ 65 g/ L). The inset shows the voice coil (1) and ferrofluid (2) positioned between the magnetic poles.

decisive contribution to heat transport. When a magnetic field is applied, the correlated motion in particle gas reduces the mass transport, or simply, the superparamagnetic state reduces the entropy when the magnetic field is exerted to it. An interesting result is the decrease of thermal conductivity with increasing mass of nanoparticles, which is hard to explain by the existing models and theories. Ferrofluids are good examples of Brownian motion in the potential presented in the well known Kramers problem;[10] this problem may be elucidated more properly in future work on the subject.

An appreciable reduction in thermal conductivity with the magnetic field somewhat reduces the range of ferrofluids application in loudspeakers. In addition, in high power loudspeakers, the magnetic fields in question are achieved on the surface of the coil wire, which in turn results in modulation of thermal conductivity and of the rate of heat removal from the voice coil. This may cause additional distortions in sound reproduction.

In conclusion, the paper has presented the preparation ingredients of ferrofluids carrying nanoparticles $CoFe_2O_4$ and γ-Fe_2O_3 and the magnetic field dependence of thermal conductivity.

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SAŽETAK

Mjerenje termičke vodljivosti ferofluida baziranih na nanočesticama $CoFe_2O_4$ i γ-Fe_2O_3

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Magnetske nanočestice $CoFe_2O_4$ i γ-Fe_2O_3 (8–15 × 10^{-9} m) razlučene su u vodi i n-dekanu koji služe kao nosači. Na tako dobivenim ferofluidima mjerene su termičke vodljivosti u magnetskom polju i na temperaturi od 25 °C. S povećanjem magnetskog polja od 2–3 × 10^{-2} T termičke vodljivosti opadaju, nakon čega su, za veća polja, neovisne o istima. Razmatrana je važnost ovisnosti termičke vodljivosti ferofluida o magnetskom polju s obzirom na mogućnost njihove primjene u zvučnicima.