

Thermomagnetic characterization of organic-based ferrofluids prepared with Ni ferrite nanoparticles

Mercedes Arana^{1,*}, Paula G. Bercoff¹, Silvia E. Jacobo²

¹*Facultad de Matemática, Astronomía, Física y Computación (FaMAF), Universidad Nacional de Córdoba. IFEG, CONICET. Medina Allende s/n, Ciudad Universitaria, Córdoba, Argentina.*

²*DiQuiMMAI, Facultad de Ingeniería, Universidad de Buenos Aires. INTECIN, CONICET. Av. Paseo Colón 850, Buenos Aires, Argentina.*

* Corresponding author: Mercedes Arana

E-mail: mercedes.arana@labh2.coppe.ufrj.br

Tel.: +55(21)39388791

Fax: +55(21)39388791

† Current address: Coppe – Instituto Alberto Luiz Coimbra de Pós-Graduação e Pesquisa de Engenharia, Universidade Federal do Rio de Janeiro, Centro de Gestão Tecnológica CGTEC-CT2, Rua Moniz Aragão N° 360, Bloco 1, Ilha do Fundão - Cidade Universitária, CEP: 21941-594, Rio de Janeiro, RJ, Brasil

Abstract

In this work, a thermomagnetic characterization of kerosene-based ferrofluids (FFs) prepared with Ni-ferrite nanoparticles (NPs) is performed by measuring their thermal conductivity and diffusivity coefficient enhancements. The particles were synthesized by high-energy ball milling, as an alternative to the most commonly chosen NPs synthesis methods for FFs. The action of an applied magnetic field on the FF increases the thermal conductivity and diffusivity due to cooperation between the NPs, as it agglomerates them favoring chain-like and clusters formations. It was found that the heat capacity of the studied FFs decreases under the application of a magnetic field. The obtained results for thermal conductivity of FFs under magnetic fields were fitted by a gas-compression model that considers NPs agglomerates in the fluid.

Keywords: Ni-ferrite, High-energy ball-milling, Ferrofluid; Thermomagnetic properties; Thermal conductivity; Diffusivity

1. Introduction

Ferrofluids (FFs) are considered advanced functional materials as they can be used to tailor the outcome in different devices by the action of an applied magnetic field. The specific properties of the FFs' free surfaces in presence of external magnetic fields are related to magnetoviscous and magnetorheologic effects [1]. In particular, during the last decade, the use of FFs as a heat-transfer medium has attracted much interest [2,3] because when the FFs are put under the influence of a magnetic field, not only their magnetic and rheological properties drastically change, but also their thermal properties. The involved processes are usually very fast [4] and, in general, reversible [5,6].

The possibility of inducing and controlling the heat transfer and the flux of fluid processes with a magnetic field, opened a window for a huge spectrum of promising applications, including devices such as thermo-siphons for technologic purposes, coolers of high power electric converters, and magnetically controlled heat-transfer devices in energy conversion systems [7].

The use of nanoparticles (NPs) for increasing the heat transfer of liquids offers several advantages [8] in comparison to the use of conventional fluids (non-magnetic nanofluids). One of them is the possibility of avoiding the implementation of complex devices with removable parts (commonly used for energy conversion and cooling devices) because a huge current of FF can be generated by temperature gradients and non-uniform magnetic fields. Therefore the thermophysical properties of FFs, such as thermal conductivity and viscosity can be modified by applying external magnetic fields [1-3,9].

Conventional liquids used for heat-transfer devices (water, oil, ethylene glycol, kerosene and others) can be a good choice for advanced applications if magnetic NPs are incorporated, but additional requirements are needed, such as high thermal conductivity and thermal expansion coefficient, low heat capacity, among others.

The thermal conductivity of different nanofluids -appropriate for heat transfer devices- has been investigated as a function of the carrier-liquid, the material of dispersed NPs, the NPs size distribution and the volumetric concentration of the FF, among other parameters. Several authors, such as Patel et al. [10], have measured the thermal conductivity (k) of nanofluids, finding that it is strongly modified by different parameters, such as concentration (volumetric fraction of NPs in the fluid) and those of the NPs dispersed in the fluid, such as size and composition. Besides, several studies (see, for

instance the work of Phillip et al. [11]), have demonstrated important enhancements in the conductivities of nanofluids prepared with magnetic NPs after applying magnetic fields [12-15].

Magnetic NPs of metallic oxides such as Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ and Mn, Zn, Co or Ni ferrites are the most used ones in FFs due to their good chemical stability and high saturation magnetization. Magnetic NPs of metallic oxides are usually prepared by chemical methods such as sol-gel and co-precipitation, by microemulsions and phases reduction [3, 16,17]. High-energy ball milling has also been successfully used to produce ferrite nanoparticles [18-23], and despite some controversy regarding the disadvantages of the method, it has proved to be a good alternative to the traditional chemical synthesis for many applications [19]. This technique allows obtaining significant amounts of the desired materials in relatively short milling times and it is effective for producing low-temperature solid-state reactions.

In our previous work [24], FFs prepared with Ni-ferrite (NiFe_2O_4) NPs synthesized by sol-gel were investigated, reaching enhancements in thermal conductivity of 50 % under applied magnetic fields. We showed that if Gd ions are incorporated as doping element in the spinel structure, this modification increases the thermal conductivity of FFs up to 60% with an applied field of 400 Oe [24], due to the well-known magnetocaloric effect of Gd.

Although it is known that the most appropriate FFs for some biological applications are those prepared by chemical methods, mainly because of the narrow size distribution of the particles, this draw-back does not seem to be relevant for heat transfer applications. In this sense, the milling is an alternative low-cost technique for large-scale NPs production as up to 5 g of nanometric powder can be obtained in short time one-step procedures. The mechanical process favors the formation of smaller (nanostructured) particles due to the collisions of the balls with the material and grinding bowls, obtaining in most cases a wide size distribution with some tendency to NPs agglomeration.

In this work, an organic-based FF was prepared with Ni-ferrite NPs synthesized by high-energy ball milling, using kerosene as organic carrier. This fluid was chosen because of its relatively high flash point and autoignition temperature (between 37 and 65 °C and 220 °C, respectively) which makes its use less risky than other solvents. Another advantages for using kerosene as a carrier are its commercial availability, long scale and industrial production, its versatility, chemical stability and low cost.

The aim of this work is to study the thermal variables –thermal conductivity and diffusivity, and heat capacity– of the prepared FFs under applied magnetic fields for possible applications in heat-transfer devices.

2. Materials and Methods

2.1. Synthesis of Nanoparticles

Ni ferrite NPs were synthesized in a high-energy ball-mill using NiO and Fe_2O_3 oxides as precursors, in stoichiometric amounts according to the reaction: $\text{Fe}_2\text{O}_3 + \text{NiO} \rightarrow \text{NiFe}_2\text{O}_4$. The milling was performed at 700 r.p.m. in stainless steel bowls with 7 WC balls, a ball-to-powder mass ratio of 35, and milling time of 20 h. This milling time is of the same order as the time reported by other authors for the synthesis of similar systems [25,26]. The obtained powder was labeled M.

2.2. Preparation of Ferrofluids

For preparing the FFs, the following substances were used: deionized milliQ water, sodium hydroxide (25 % w/w), oleic acid, nitric acid (10 % v/v), kerosene, acetone, and distilled water. 200 mg of Ni ferrite (NiFe_2O_4) were weighted (sample M) and were suspended in 20 mL of deionized water. Ten drops of sodium hydroxide solution were added up to pH 10 and the final solution was sonicated for 5 minutes. Stirring with a thin glass bar, 200 mg of oleic acid were added. Then, the system was heated at 95 °C while stirring and keeping the pH in 10. After cooling the solution, a diluted nitric acid solution (10 % v/v) was added up to pH 6. For retaining the magnetic part of the solution, a magnet was located at the bottom of the container. The remaining was washed 4 – 5 times with water at 50 °C and twice with 1 mL of acetone for removing the water excess. Finally, the particles were dispersed in kerosene and sonicated during 3 h. Two FFs concentrations were prepared, 5 and 10 % v/v which were labeled F-M5 and F-M10, respectively. Both samples remained stable for months.

2.3. Characterization Techniques

X-Ray diffractograms were measured in a Philips diffractometer using Cu $K\alpha$ radiation. Spectra were collected in the 2θ range 20-70°, with a step-size of 0.02°, at a counting rate of 4 seconds per step. The morphology of samples was examined by Scanning Electronic Microscopy (SEM), and the images were analyzed with *ImageJ* software [27]. The

magnetic properties of samples compacted in 1-2 mm thick disks were measured at room temperature (RT) in a vibrating sample magnetometer LakeShore 7200 with a maximum applied field of 1.5 T (15 kOe).

The transient hot-wire method [21-23] was used to determine the thermal conductivity and diffusivity of the prepared FFs. For this purpose, a home-made device was designed with dimensions and characteristics such that it can be used under a magnetic field of different intensities. The heat capacity of the FFs was also determined.

2.4. Thermal variables

The increment in conductivity can be calculated as $I = [(k_{FF} - k_0)/k_0] \cdot 100\%$ being k_{FF} and k_0 the FF and the kerosene thermal conductivities respectively, while the relative-to-kerosene diffusivity coefficient can be calculated as $\alpha_r = \alpha_{FF}/\alpha_0$ where α_{FF} and α_0 are the diffusivity coefficients of FF and kerosene, respectively.

For applications in heat-transfer devices, the results of thermomagnetic characterization can be properly represented by some parameters of particular interest, such as: thermal conductivity enhancement at zero field $I(H=0)$, maximum enhancement of thermal conductivity I_{max} , magnetic field for which the maximum increment is produced, H_k ; relative thermal diffusivity coefficient at zero field $\alpha_r(H=0)$; the maximum diffusivity coefficient α_{rmax} and the field for which maximum diffusivity value is produced H_{α} .

The heat capacity of prepared FFs can be calculated using the expression $C_p = k/(\rho \cdot a) = k/[(x\rho_{NP} + (1-x)\rho_f) \cdot a]$, where ρ , ρ_{NP} and ρ_f are the FF, NPs and base fluid densities respectively, and x is the volume fraction of NPs for each magnetic field intensity. C_{pr} is the relative-to-kerosene heat capacity, calculated as the ratio of the heat capacity of the FF to kerosene.

3. Results and discussion

3.1 NPs characterization

Figure 1 (a) shows the X-Ray diffractogram of the obtained powder after the milling. The diffraction pattern was indexed using JCPDS cards N° 10-0325 for Ni-ferrite and N° 73-0603 for hematite. A small percentage of hematite Fe_2O_3 ($\leq 10\%$) is noticed, which indicates that the reaction was not complete. Usually, the presence of this kind of secondary phase can be eliminated either by further milling or an adequate thermal treatment [28,29]. However, in this case, we decided to use the as-milled material without further treatments in order to preserve the obtained crystal size.

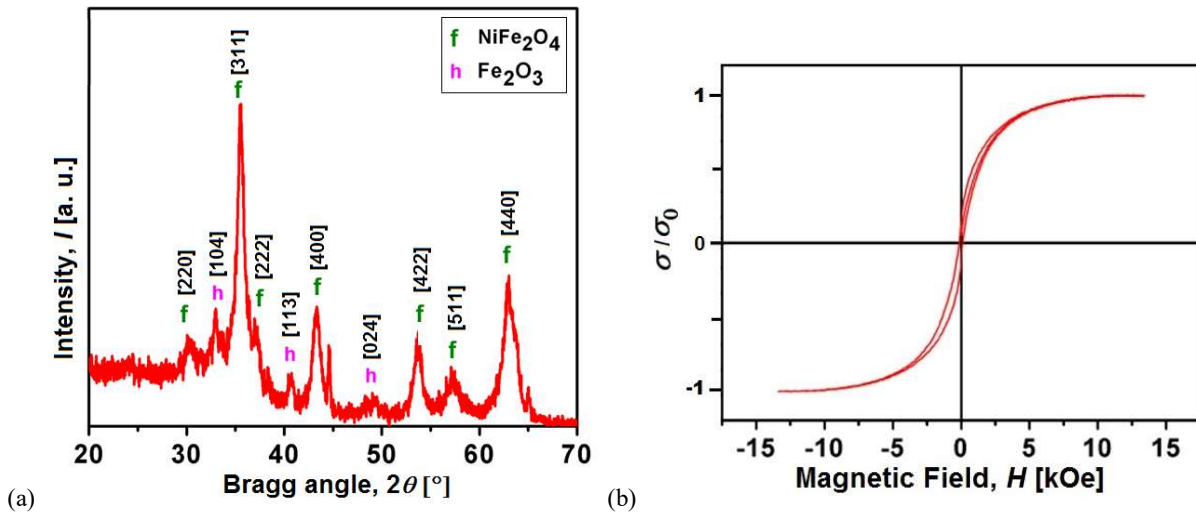


Figure 1: X Ray diffractogram (a) and relative magnetization vs. magnetic field curve (b) of the synthesized powder.

Saturation magnetization M_s of Ni ferrite NPs was obtained from the hysteresis loop shown in Figure 1 (b) after subtracting the paramagnetic contribution of hematite. For the prepared NPs, M_s takes the value of (5.8 ± 0.1) emu/g, which is approximately 10 times lower than M_s for Ni ferrite particles of larger sizes [30] and that of bulk (50 emu/g [31]). However, such a low M_s value was also obtained by other authors in a previous work on a Ni ferrite system with similar NPs sizes [32].

In Figure 2, a SEM image of Ni-ferrite synthesized powder and the corresponding particle size histogram -constructed from several micrographs- are presented.

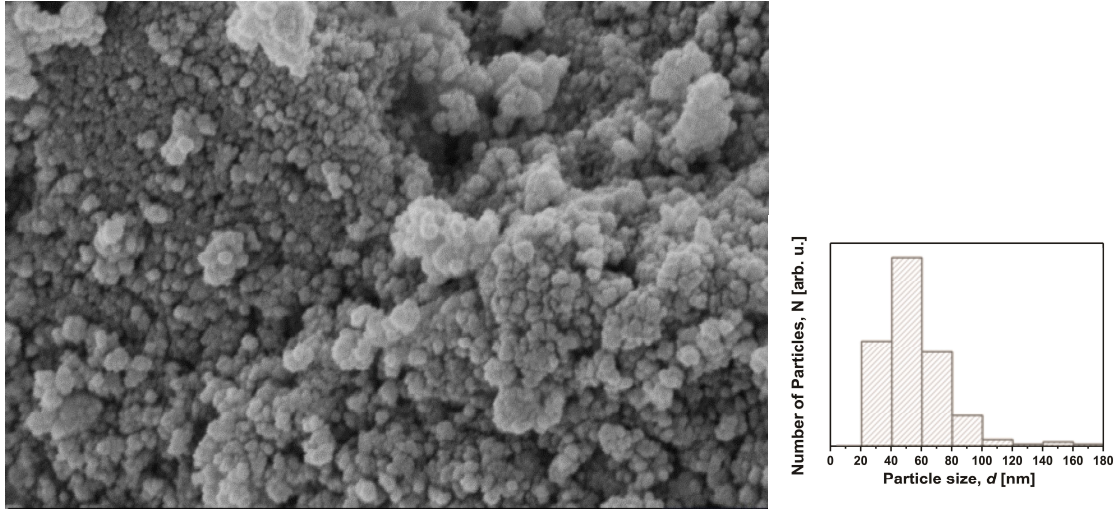


Figure 2: SEM micrograph of sample M and particle size distribution histogram.

The average particle size of powder M is 50 nm with a dispersion of 10 nm. As it is clear from the figure, the particle size distribution is homogeneous and, although mostly spherical NPs of uniform morphology can be observed, a minor quantity of NPs of irregular shape cannot be discarded.

The magnetization M vs applied field H behavior of sample M (shown in Figure 1b) is typical of a superparamagnetic material, with negligible coercivity and relatively low saturation magnetization, which is expected for NPs of Ni ferrite with this mean size and the presence of a secondary phase.

3.2. Ferrofluids' thermal conductivity and diffusivity under applied magnetic fields

Figure 3 shows the relative thermal diffusivity coefficient (a) and the increment in thermal conductivity (b) of F-M5 and F-M10, as a function of the applied magnetic field. The obtained values of thermal variables are summarized in Table 1, along with reported data for similar FFs.

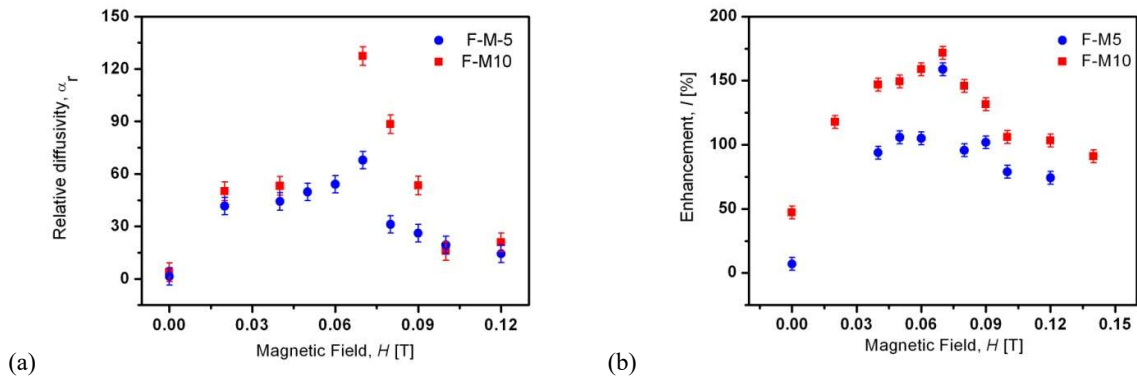


Figure 3: Relative diffusivity (a) and enhancement of thermal conductivity (b) of F-M5 and F-M10 as functions of the applied magnetic field.

It is clear from Figure 3 that increasing the magnetic field produces enhancements in both the thermal conductivity and the diffusivity coefficient of FFs up to a maximum, and then they diminish. This behavior is observed for both concentrations. In the absence of magnetic field, the presence of NPs in the fluids slightly improves the thermal properties of the organic carrier, as every enhancement is positive and every relative diffusivity coefficient is greater than 1. This increasing and decreasing behavior as a function of the magnetic field has already been observed by Philip et al. [11] in aqueous FFs with magnetite NPs.

The modification in thermal conductivity and diffusivity of FFs as a function of the magnetic field can be explained by considering the interaction between the NPs. In absence of magnetic field, every particle of a FF acts as an individual

magnet, randomly oriented. The particles are uniformly dispersed in the fluid, due to the coating of their surface and the stabilization treatments performed during the FF preparation. The magnetic moments of the NPs are randomly oriented because the thermal energy is considerably higher than the dipolar interaction between the particles and this is only influenced by the Brownian motion [11, 33]. When applying the magnetic field on the fluids, the Zeeman interaction acts to orient the magnetic moments, aligning them and forming doublets, triplets and chains aligned to the field direction and of lengths that increase with the magnetic field [11].

The number of magnetic particles that tend to self-align in the direction of the magnetic field significantly grows with the increase of the field intensity and significant enhancements from 46 to 173 % can be observed. When the applied field increases, several chains are linked forming bigger structures -as clusters- and liberate more liquid zones (with lower thermal conductivity than the NPs), diminishing the thermal diffusivity and conductivity.

It should be noted that in this simple model the NPs are supposed to be monodisperse.

When applying the magnetic field, the spherical NPs with irregular surfaces can be re-organized in different arrangements, increasing the cooperation between each other. In this way, the particles fill the free liquid space, contributing with a higher conductivity.

Table 1. FFs' description, thermal conductivity and relative thermal diffusivity enhancements at zero field, maximum thermal conductivity enhancements and relative diffusivity values, and magnetic fields for which the maximum increments are produced.

NPs@coating/fluid particle size	Ferrofluid concentration [% v/v]	$I(H=0)$ [±5%]	I_{max} [±5%]	H_k [±0.002T]	$\alpha_r(H=0)$ [± 5]	$\alpha_{rmax}[\pm$ 5]	H_α [±0.002T]	Ref
NiFe ₂ O ₄ @OleicAcid/kerosene 50 nm	5	4	160	0.070	2	68	0.070	This work
NiFe ₂ O ₄ @OleicAcid/kerosene 50 nm	10	48	173	0.070	3	127	0.070	
NiFe ₂ O ₄ @OleicAcid/kerosene 50 nm	5	29	46	0.140	1.8	-	-	Jacobo et al. [24]
	10	25	48	0.050	1.4	-	-	
Gd substituted- NiFe ₂ O ₄ @OleicAcid/kerosene 50 nm	5	20	54	0.100	1.0	-	-	
	10	18	63	0.020- 0.060	2.2	-	-	

According to Table 1, the obtained results of thermal conductivity and diffusivity measurements indicate that the high-energy ball-milled Ni-ferrite NPs significantly improve the thermal properties of pure kerosene; see for instance that the thermal conductivity enhancement of a 10 % concentrated fluid is 48 % in absence of magnetic field. This first result indicates that this enhancement is mainly produced by the incorporation of NPs into the fluid.

In this work, the conductivity enhancement with an applied field of 0.07 T is 160% for F-M5, and 173% for F-M10. These values are higher than those obtained for a similar system, in which the fluid is also prepared with kerosene and Ni-ferrite NPs, but with particles synthesized by a chemical method [24]. As far as we know from the available literature, no other authors have investigated the actual thermal properties of ferrofluids prepared with Ni-ferrite NPs.

Other works about fluids prepared with Mn-Zn ferrite of smaller particle sizes report lower enhancements than the ones herein studied for similar magnetic field intensities [34].

3.3. Ferrofluids' heat capacity under applied magnetic fields

The calculated heat capacity as a function of the applied field is presented in Figure 4 for F-M5 and F-M10.

Kerosene heat capacity decreases after incorporating the NPs, since at zero field the C_{Pr} is lower than 1. It also diminishes when the FFs concentration is increased from 5 to 10 % v/v. A remarkable effect is produced in both samples when applying the magnetic field, as the C_{Pr} value decreases to almost zero and remains almost constant while increasing the magnetic field intensity.

The average C_{Pr} value of F-M under an applied magnetic field is (0.05 ± 0.03) for both the concentrated FF and the diluted one. As far as we know, no C_p measurements or calculations in presence of magnetic field have been done up to present for similar systems.

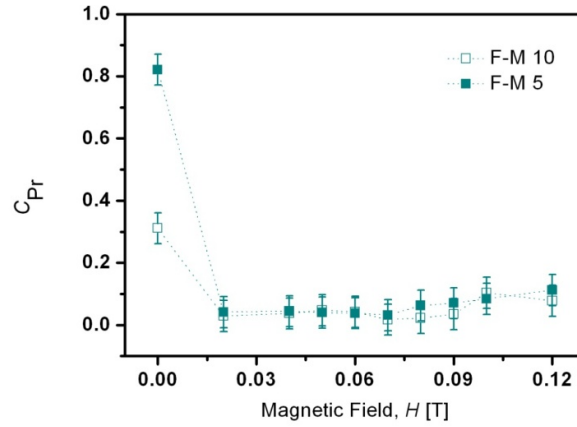


Figure 4: Relative heat capacity of F-M5 and F-M10, as a function of the applied magnetic field.

3.4. Modeling the ferrofluid's thermal conductivity

A static suspension of nanosized particles is different from that of micro-sized one, since the particles are constantly moving randomly, even if the bulk fluid is steady. For this reason, there is a fundamental difference in heat-transfer mechanisms in nanofluids associated to dynamical effects (in absence of magnetic field). Several mechanisms are responsible for heat conduction in nanofluids (see, for instance, the works of Ji-Hwan Lee [35] and Xiang Qi Wang [36]). Maxwell's effective average field classic model assumes that thermal conductivity of FFs is dependent on the NPs volumetric fraction (φ) in the low-concentration range when the ratio of NPs thermal conductivity to that of the fluid is high enough. According to this model, the thermal conductivity k of a nanofluid with NPs and fluid thermal conductivities k_p and k_f , respectively, is given by:

$$k = k_f \cdot \left(\frac{k_p + 2k_f + 2\varphi \cdot (k_p - k_f)}{k_p + 2k_f - \varphi \cdot (k_p - k_f)} \right) \quad (1)$$

On the other hand, different experimental results indicate that thermal conductivity of nanofluids also depends on other parameters such as particle size, fluid temperature, and pH, among others. Taking into account the results obtained in this work, it is readily noticed that the FFs' thermal conductivity also depends on the NPs concentration, morphology and roughness of NPs, as well as the intensity of the applied magnetic field (which is directly related to the magnetic interaction between NPs).

Several authors have proposed new concepts and mechanisms behind the nanofluids thermal conductivity behavior in order to consider the influence of every involved physical parameter in absence of magnetic field, modifying Maxwell expression.

Hamilton and Crosser [37], have proposed a model for solid-liquid mixtures when NPs are not perfect spheres. Yu *et al.* [38] experimentally showed the existence of an ordered layer of liquid molecules in the solid-liquid interface, which had been predicted in the 80's. This nanolayer structure was introduced by Keblinski *et al.* [39], who estimated the upper limit in conductivity with the effect of this thin layer, assuming that the thermal conductivity of the liquid nanolayer is the same as that of the solid NP. Also, Yu and Choi [40] have proposed that the nanolayer concept acts as a thermal bridge between the NP and the liquid in bulk. Based on this new mechanism, Yu and Choi developed a modified Maxwell model for the effective thermal conductivity of nanofluids that contain spherical nanoparticles covered by an ordered layer. They explained the thermal bridge concept with non-spherical nanoparticles and renewed the Hamilton-Crosser model [41] with the following expression for the thermal conductivity of FFs:

$$k = k_f \cdot \left(\frac{k_{pe} + 2k_f + 2\varphi \cdot (1-\beta)^3 (k_{pe} - k_f)}{k_{pe} + 2k_f - \varphi \cdot (1+\beta)^3 (k_{pe} - k_f)} \right) \quad (2)$$

In this expression, $\beta = h/r_p$ is the ratio between the nanolayer width and the original radius of the NP (r_p), and k_{pe} is the effective conductivity of the NPs, given by:

$$k_{pe} = k_f \cdot \left(\frac{2(1-\gamma) + (1+\beta)^3 (1+2\gamma)\gamma}{(\gamma-1) + (1+\beta)^3 (1+2\gamma)} \right)$$

In the last expression, γ is the ratio between the NPs' and the coating nanolayers' thermal conductivities.

It is worth mentioning that the effective average field assumes that the NPs are in a steady state in the fluid, therefore it cannot explain the k value dependence of temperature and particle sizes. The Brownian motion, by which the NPs move in the liquid and facilitate the direct solid-solid heat transfer between particles, is expected to increase the thermal conductivity of nanofluids. It is believed that the Brownian motion contribution to the thermal conductivity increases with the temperature and decreases with particle sizes. Shukla *et al.* [42] have proposed the following equation for thermal conductivity of FFs, based on the Brownian motion of NPs in an homogenous liquid, using the Maxwell model:

$$k = \left(\frac{k_p + 2k_l + 2\varphi \cdot (k_p - k_l)}{k_p + 2k_l - \varphi \cdot (k_p - k_l)} \right) + \frac{A\varphi \cdot (T - T_0)}{\mu r_p^4} \quad (3)$$

where A is a constant whose value was adjusted with experimental information and takes the value 7×10^{-36} , μ is the dynamic viscosity coefficient and T_0 is a reference temperature equal to 294 K. These authors found a reasonable agreement between predicted values and experimental data. The first term of the sum represents the Maxwell macroscopic model contribution, while the second one represents that of Brownian motion of NPs.

3.4.1. Thermal Conductivity at $H=0$

Having in mind the above-described state of the art, we propose a thermal conductivity expression as a function of the volume concentration in absence of magnetic field predicted by the mentioned different models, combining Yu and Choi [34] model with the contribution proposed by Shukla [42]. This new expression results:

$$k = \left(\frac{k_{pe} + 2k_l + 2\varphi \cdot (1-\beta)^3 (k_{pe} - k_l)}{k_{pe} + 2k_l - \varphi \cdot (1+\beta)^3 (k_{pe} - k_l)} \right) + \frac{C\varphi \cdot (T - T_0)}{\mu r^4} \quad (4)$$

This equation for thermal conductivity of FFs considers both the nanolayer that coats the magnetic NPs (oleic acid in this case) and the Brownian motion of the NPs in the fluid.

In Figure 5, the Maxwell, Yu and Choi model predictions (Equations 1-3) of thermal conductivity are presented for the studied FF (sample F-M), and the model proposed in this work (Equation 4) together with the experimental data.

Calculations were performed with the following values of physical parameters:

- Ni ferrite thermal conductivity: $k_p = 8.75 \text{ W/}^\circ\text{Cm}$ [43]
- Oleic acid nanolayer thermal conductivity: $k_{oleic} = 0.145 \text{ W/}^\circ\text{Cm}$ [44]
- Oleic acid nanolayer thickness: $h = 2 \text{ nm}$
- Kerosene dynamic viscosity coefficient: $\mu = 1.5 \cdot 10^{-4} \text{ kg/ms}$
- Ratio between surfactant (oleic acid) and Ni ferrite NPs thermal conductivities: $\gamma = 0.017$
- Room temperature during the experiments: $T = 25 \text{ }^\circ\text{C}$ (298 K)

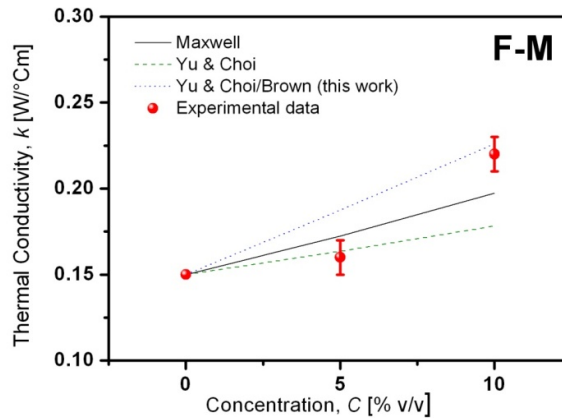


Figure 5 Thermal conductivity data for the two studied volumetric concentrations and thermal conductivity predicted by Maxwell [45] (solid black line) Yu and Choi [40] (dashed green line) and this work (dotted blue line).

From Figure 5, it is clear that the proposed model by Yu and Choi can explain the behavior of F-M5, while for F-M10, the proposed model in Equation 4 is the best choice. This was an expected result, since increasing the particles concentration makes them closer one to each other and the collisions produced by Brownian motion notably increase,

thus favoring the thermal conduction. Taking into account the oleic acid layer -whose thermal conductivity is lower than that of kerosene- explains that the conductivity proposed by Yu and Choi is smaller than that predicted by Maxwell's model.

3.4.2. Thermal Conductivity vs. H

In presence of a magnetic field, the NPs aggregation cannot be overseen in order to consider all the different mechanisms that explain thermal conductivity. Even in absence of magnetic field, aggregation is a property inherent to the particles, (either dispersed in a liquid or in dry powder), due to Van der Waals forces. Keblinski *et al.*[39] have conceptualized the NPs clustering as a mechanism of thermal conductivity enhancement, assuming that NPs clusters provide local percolation paths for fast heat transfer and enhance the volumetric fraction of NPs. Besides, Wang *et al.* [46] have developed a fractal model for predicting the conductivity of nanofluids containing NPs clusters. Prasher *et al.* [47, 48] have studied the aggregation effects of nanofluids over k and showed that the time-aggregation constant quickly decreases with smaller NPs sizes and that enhancements in conductivity are higher when increasing the aggregation level, stabilizing the fluids to an optimum aggregation level. Nevertheless, Xuan *et al.* [49] simulated the Brownian motion and NPs aggregation and showed that NPs aggregation reduces the nanofluids conductivity, because the random motion of aggregates is lower than that of the corresponding to free particles. The last-described behaviors indicate that there is a competition between NPs size and the number of clusters, with respect to the size and the number of free NPs in the liquid, in absence of magnetic field. However, this aggregation can be determinant for increments in conductivity of fluids if they are under an applied magnetic field, since it orientates and aggregates the particles according to their intensity and orientation, favoring an enhancement in conductivity.

In their work, Nkurikiyimfura *et al.* [50] explain the observed enhancements in thermal conductivity of magnetite NPs FFs based in oil as a function of the magnetic field, with an aggregation model in which the volumetric concentration of the FF is enhanced by the applied magnetic field. The used model was proposed by Jian Li *et al.* [51], and it considers the similarity between the magnetic NPs aggregation and a gas compression. In this way, the observed behavior of thermal conductivity as a function of the applied field was successfully explained. Those authors proposed that the FFs behave as a nano-aggregate fluid under a magnetic field, and have a volumetric concentration of aggregates given by:

$$\varphi_a = (\varphi_m - \varphi_h) \cdot \tanh(\kappa\varphi\varepsilon) + \varphi_h \quad (5)$$

where φ_m is the maximum concentration of NPs, κ is the compression parameter, ε is the Langevin effective parameter (defined as the ratio of NPs interaction energy to the local magnetic field, and thermal energy $k_B T$) and φ_h is the NPs hydrodynamic volume fraction:

$$\varphi_h = \varphi \left(\frac{d+\delta}{d} \right)^3$$

with δ the NPs nanolayer thickness and d their diameter.

The local magnetic induction is given by:

$$B = \mu_0 \cdot (H + (4\pi M_L/3))$$

with M_L given by the expression:

$$M_L = \varphi M_S L(x)$$

and x by:

$$x = \mu_0 \pi M_S d^3 H / 6 k_B T$$

where L is the Langevin function ($L(x) = \tanh(x) - (1/x)$).

It should be noted that this model can explain the thermal conductivity behavior as a function of magnetic field only up to the maximum value, because then saturation is reached and conductivity starts decreasing due to other physical processes, such as decantation because of agglomeration, since increasing the magnetic field promotes NPs clustering and consequently the Van der Waals forces and are no longer strong enough to compete with gravity.

In order to explain the observed enhancements in the thermal conductivity of the studied FFs with increasing magnetic field intensity, the aggregation gas model proposed by Li *et al.* [51], was used. The NPs aggregates concentration was calculated using Equation (4) with $\varphi_m = 0.638$ [51] and the Langevin magnetization of NPs of average size. For calculating the thermal conductivity, the Maxwell model of a FF with aggregates of concentration φ_a , was used. The fitting parameter was the compressibility coefficient, κ .

In Figure 6, the experimental values of the measured thermal conductivity for F-M5 and F-M10 are presented, together with the predicted behavior by Maxwell model for aggregates as a function of magnetic field intensity.

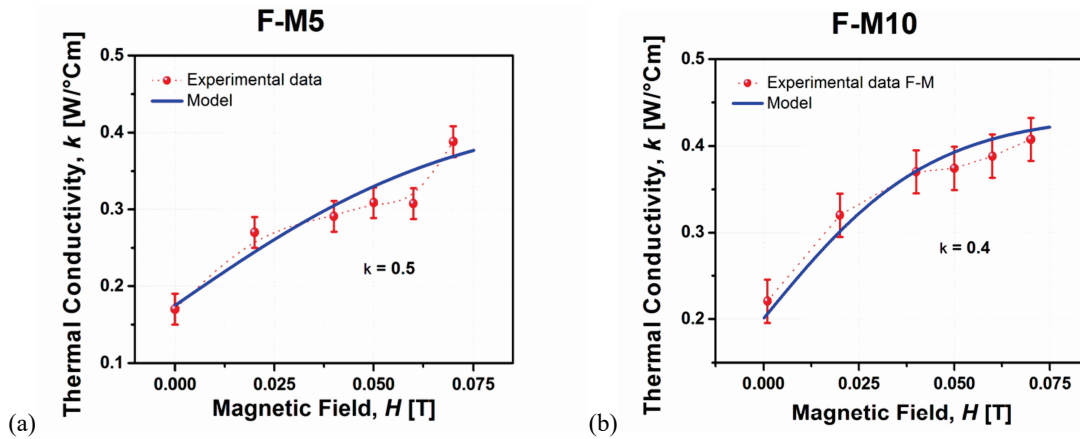


Figure 6: Experimental and theoretical values of thermal conductivity for F-M5 and F-M10 as function of the magnetic field. The blue line corresponds to Maxwell model [45] modified with Jian Li *et al* equation [51].

These graphs indicate that the proposed model can properly and successfully explain the obtained results. A similar compressibility coefficient was obtained for both fluids, possibly because of the strong interaction between the NPs.

The studied physical parameters of FFs can be easily controlled and selectively modified in the lab, according to the desired applications. It is very useful to have this in mind, as enhancements in conductivity favor a higher heat delivery/release by temperature and distance units; increments in diffusivity are related to higher cooling/heating velocities; and a heat capacity decrease allows a less energy-consuming temperature reduction.

The thermal conductivity and diffusivity and the heat capacity of prepared FFs are maximized in every case with fields lower than 0.1 T, being those values easily accessible with commercially available permanent magnets. Heat transfer devices can be simply developed with the prepared FFs, by placing the object that needs to be cooled/heated in mutual contact with the FF and an appropriate arrangement of magnets that favors the heat conduction/dissipation process.

The discovery achieved by Philip [11], and Shima *et al.* [52], showed that magnetically well-organized nanofluids can behave as intelligent multifunctional materials that can work as a refrigerant and also as an *on-off* switch, offering applications of great interest in microelectromechanic (MEMs) fluid devices, and others based in miniaturization.

4. Conclusion

The thermal conductivity of the FFs herein prepared, with NPs synthesized by milling, was explained in first approximation (in absence of magnetic field) by the Maxwell classical model. Other models were also compared, such as that of Yu and Choi, which considers the surfactant as a fluid nanolayer coating the NPs, and an expression that combines this last one with Brownian motion.

The conductivity and diffusivity of FFs are enhanced when increasing the concentration and the applied field intensity. The measured thermal conductivity enhancements of FFs reached 170 % and the achieved thermal diffusivity enhancements were up to 70 times the value of kerosene without particles, both reached when applying fields of 0.07 T, easily obtainable with commercially available permanent magnets.

The thermal conductivity of the prepared FFs as a function of the applied magnetic field was successfully explained with a compression-gas model that proposes that the magnetic field produces a fluid of NPs nanoaggregates.

The heat capacity of the prepared FFs was calculated and it was found that it decreases when incorporating the particles, and even more in presence of magnetic field.

Our work shows that organic-based FFs with Ni-ferrite NPs are an excellent choice for heat transfer devices, considering their low-cost, simple synthesis procedure and optimum thermal properties.

Acknowledgements

This work was partially funded by Secyt-UNC and CONICET. The authors also thank LAMARX for granting access to the SEM facility and Daniel Felix from FaMAF Electronic Department for collaborating in the realization of the transient hot-wire device.

References

- [1] Odenbach S, Thurm S. Ferrofluids magnetically controllable fluids and their applications/ Magnetoviscous Effects in Ferrofluids. Lect. Notes Phys., vol. 594, Springer; 2002, p. 185–201.
- [2] Bayat N, Nethe A, Guldbakke JM, Hesselbach J, Naletova VA, Stahlmann HD, et al. Technical applications. In: Odenbach S, editor. Colloid. Magn. Fluids, vol. 763, Berlin, Heidelberg: Springer Berlin Heidelberg; 2009, p. 1–72. doi:10.1007/978-3-540-85387-9.
- [3] Charles SW. The preparation of magnetic fluids. In: Odenbach S, editor. Ferrofluids, vol. 594, Berlin, Heidelberg: Springer Berlin Heidelberg; 2002, p. 3–18. doi:10.1007/3-540-45646-5.
- [4] Berkov DV, Gorn NL. & Stock D. Remagnetization processes in ferrofluids: numerical simulations using the Langevin dynamics, *Magnetohydr.* 2003; 39, No. 1, p. 97-103.
- [5] Kellner R. & Kohler W. Short-time aggregation dynamics of reversible light induced cluster formation in ferrofluids; *J Optoelectronics. Adv. Mat.* 2007;9, No. 11, p. 3427–3430.
- [6] Laskar JM, Philip J, Raj B. Experimental investigation of magnetic-field-induced aggregation kinetics in nonaqueous ferrofluids. *Phys Rev E Stat Nonlin Soft Matter Phys.* 2010; 82 (2 Pt 1):021402.
- [7] E. B. Heat and mass transfer phenomena. In: Odenbach S, editor. Ferrofluids Magn. Control. Fluids Their Appl., Berlin, Heidelberg: New York: Springer-Verlag; 2002, p. 185–201.
- [8] Kuzubov AO, Ivanova OI. Magnetic liquids for heat exchange. *J Phys III* 1994;4:1–6. doi:10.1051/jp3:1994108.
- [9] Philip J, Shima PD, Raj B. Evidence for enhanced thermal conduction through percolating structures in nanofluids. *Nanotechnology* 2008;19:305706. doi:10.1088/0957-4484/19/30/305706.
- [10] Patel HE, Sundararajan T, Das SK. An experimental investigation into the thermal conductivity enhancement in oxide and metallic nanofluids. *J Nanoparticle Res* 2009;12:1015–31. doi:10.1007/s11051-009-9658-2.
- [11] Philip J, Shima PD, Raj B. Enhancement of thermal conductivity in magnetite based nanofluid due to chainlike structures. *Appl Phys Lett* 2007;91:203108. doi:10.1063/1.2812699.
- [12] Djurek I, Djurek D. Thermal Conductivity Measurements of the CoFe₂O₄ and g-Fe₂O₃ based Nanoparticle Ferrofluids. *Croat Chem ACTA* 2007;80:529–32.
- [13] Fu HL, Gao L. Theory for anisotropic thermal conductivity of magnetic nanofluids. *Phys Lett A* 2011;375:3588–92. doi:10.1016/j.physleta.2011.08.026.
- [14] Philip J, Shima PD, Raj B. Nanofluid with tunable thermal properties. *Appl Phys Lett* 2008;92:043108. doi:10.1063/1.2838304.
- [15] van Ewijk GA, Vroege GJ, Philipse AP. Convenient preparation methods for magnetic colloids. *J Magn Magn Mater* 1999;201:31–3. doi:10.1016/S0304-8853(99)00080-3.
- [16] Kolesnichenko VL. Synthesis of nanoparticulate magnetic materials. In: Gubin SP, editor. *Magn. Nanoparticles*, Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA; 2009, p. 25–53.
- [17] Vékás L, Bica D, Avdeev M V. Magnetic nanoparticles and concentrated magnetic nanofluids: Synthesis, properties and some applications. *China Particuology* 2007;5:43–9. doi:10.1016/j.cpart.2007.01.015.
- [18] Arana M, Jacobo SE, Troiani H, Bercoff PG. Synthesis and Characterization of Carbon-Coated Magnetite for Functionalized Ferrofluids. *IEEE Trans Magn* 2013;49:4547–50. doi:10.1109/TMAG.2013.2259805.
- [19] Arana M, Tettamanti CS, Bercoff P. Magnetite NPs@C with highly-efficient peroxidase-like catalytic activity as an improved biosensing strategy for selective glucose detection. *Electroanalysis* 2014:1–22.
- [20] McCormick PG. Application of mechanical alloying to chemical refining (overview). *Mater Trans* 1995;36:161–9.
- [21] Ding J, Miao WF, McCormick PG, Street R. Mechanochemical synthesis of ultrafine Fe powder 1995;67:3804–6.
- [22] Muroi M, Amighian J, Street R, McCormick PG, Mnfe U. Synthesis of ultrafine manganese-ferrite powders by mechanochemical processing n.d.:1091–8.
- [23] Arana M, Bercoff PG, Jacobo SE, Zélis PM, Pasquevich GA. Mechanochemical synthesis of MnZn ferrite nanoparticles suitable for biocompatible ferrofluids. *Ceram Int* 2016;42:1545–51. doi:10.1016/j.ceramint.2015.09.103.
- [24] Jacobo SE, Arana M, Bercoff PG. Gadolinium substitution effect on the thermomagnetic properties of Ni ferrite ferrofluids. *J Magn Magn Mater* 2015:1–5. doi:10.1016/j.jmmm.2015.11.047.
- [25] Bid S, Sahu P, Pradhan SK. Microstructure characterization of mechanothesized nanocrystalline NiFe₂O₄ by Rietveld's analysis. *Phys E Low-Dimensional Syst Nanostructures* 2007;39:175–84. doi:10.1016/j.physe.2007.01.005.
- [26] Bid S, Pradhan S. Characterization of crystalline structure of ball-milled nano-Ni–Zn-ferrite by Rietveld method. *Mater Chem Phys* 2004;84:291–301. doi:10.1016/j.matchemphys.2003.08.012.
- [27] Rasband W. ImageJ 2012. <http://imagej.nih.gov/ij/index.html> (accessed April 10, 2015).
- [28] Arana M. Preparación y caracterización de ferritas de Mn-Zn para diferentes aplicaciones. Universidad Nacional de Córdoba, 2011.

- [29] M. Arana, S.E. Jacobo, H. Troiani and PGBFMAF. Synthesis and Characterization of Carbon-Coated Magnetite for Functionalized Ferrofluid. *IEEE Trans Magn* 2013;49.
- [30] Journal of Magnetism and Magnetic Materials Volume 415, 1 October 2016, Pages 30–34 International Baltic Conference on Magnetism: focus on biomedical aspects.
- [31] Chappert, J. & Frankel, R. Mössbauer Study of Ferrimagnetic Ordering in Nickel Ferrite and Chromium-Substituted Nickel Ferrite. *Phys. Rev. Lett.* 19, 570–572 (1967).
- [32] Shahbaz Tehrani, F., Daadmehr, V., Rezakhani, a. T., Hosseini Akbarnejad, R. & Gholipour, S. Structural, Magnetic, and Optical Properties of Zinc and Copper-Substituted Nickel Ferrite Nanocrystals. *J. Supercond. Nov. Magn.* 25, 2443–2455 (2012).
- [33] Gavili A, Zabihi F, Isfahani TD, Sabbaghzadeh J. The thermal conductivity of water base ferrofluids under magnetic field. *Exp Therm Fluid Sci* 2012;41:94–8. doi:10.1016/j.expthermflusci.2012.03.016.
- [34] Parekh K, Lee HS. Experimental investigation of thermal conductivity of magnetic nanofluids. *Conf. Proc.*, vol. 385, 2012, p. 385–6. doi:10.1063/1.4710041.
- [35] Lee J-H, Lee S-H, Choi CJ, Jang SP, Choi SUS. A Review of Thermal Conductivity Data, Mechanisms and Models for Nanofluids. *Int J Micro-Nano Scale Transp* 2010;1:269–322. doi:10.1260/1759-3093.1.4.269.
- [36] Wang X-Q, Mujumdar AS. Heat transfer characteristics of nanofluids: a review. *Int J Therm Sci* 2007;46:1–19. doi:10.1016/j.ijthermalsci.2006.06.010.
- [37] Hamilton RL, Crosser OK. Thermal Conductivity of Heterogeneous Two-Component Systems. *Ind Eng Chem Fundam* 1962;1:187–91. doi:10.1021/i160003a005.
- [38] Yu C-J, Richter A., Datta A, Durbin M., Dutta P. Molecular layering in a liquid on a solid substrate: an X-ray reflectivity study. *Phys B Condens Matter* 2000;283:27–31. doi:10.1016/S0921-4526(99)01885-2.
- [39] Keblinski P, Phillpot S., Choi SU., Eastman J. Mechanisms of heat flow in suspensions of nano-sized particles (nanofluids). *Int J Heat Mass Transf* 2002;45:855–63. doi:10.1016/S0017-9310(01)00175-2.
- [40] Yu W, Choi SUS. The Role of Interfacial Layers in the Enhanced Thermal Conductivity of Nanofluids: A Renovated Maxwell Model. *J Nanoparticle Res* 2003;5:167–71. doi:10.1023/A:1024438603801.
- [41] Yu W, Choi SUS. The role of interfacial layers in the enhanced thermal conductivity of nanofluids: A renovated Hamilton-Crosser model. *J Nanoparticle Res* 2004;6:355–61. doi:10.1007/s11051-004-2601-7.
- [42] Shukla RK, Dhir VK. Study of the Effective Thermal Conductivity of Nanofluids. *Heat Transf. Part B*, vol. 2005, ASME; 2005, p. 537–41. doi:10.1115/IMECE2005-80281.
- [43] Nelson AT, White JT, Andersson D a., Aguiar J a., McClellan KJ, Byler DD, et al. Thermal Expansion, Heat Capacity, and Thermal Conductivity of Nickel Ferrite (NiFe₂O₄). *J Am Ceram Soc* 2014;97:1559–65. doi:10.1111/jace.12901.
- [44] Kefayati GHR. Lattice Boltzmann simulation of natural convection in partially heated cavities utilizing kerosene/cobalt ferrofluid. *IJST, Trans Mech Eng* 2013;37:107–18.
- [45] Nkurikiyimfura I, Wang Y, Pan Z. Heat transfer enhancement by magnetic nanofluids—A review. *Renew Sustain Energy Rev* 2013;21:548–61. doi:10.1016/j.rser.2012.12.039.
- [46] Wang B-X, Zhou L-P, Peng X-F. A fractal model for predicting the effective thermal conductivity of liquid with suspension of nanoparticles. *Int J Heat Mass Transf* 2003;46:2665–72. doi:10.1016/S0017-9310(03)00016-4.
- [47] Prasher R, Phelan PE, Bhattacharya P. Effect of aggregation kinetics on the thermal conductivity of nanoscale colloidal solutions (nanofluid). *Nano Lett* 2006;6:1529–34. doi:10.1021/nl060992s.
- [48] Prasher R, Evans W, Meakin P, Fish J, Phelan P, Keblinski P. Effect of aggregation on thermal conduction in colloidal nanofluids. *Appl Phys Lett* 2006;89:143119. doi:10.1063/1.2360229.
- [49] Xuan Y, Li Q, Hu W. Aggregation structure and thermal conductivity of nanofluids. *AIChE J* 2003;49:1038–43. doi:10.1002/aic.690490420.
- [50] Nkurikiyimfura I, Wang Y, Pan Z. Effect of chain-like magnetite nanoparticle aggregates on thermal conductivity of magnetic nanofluid in magnetic field. *Exp Therm Fluid Sci* 2013;44:607–12. doi:10.1016/j.expthermflusci.2012.08.024.
- [51] Jian Li, Yan Huang, Xiaodong Liu, Yueqing Lin, Lang Bai QL. Effect of aggregates on the magnetization property of ferrofluids: A model of gaslike compression n.d.
- [52] Philip J, Shima PD, Raj B. Evidence for enhanced thermal conduction through percolating structures in nanofluids. *Nanotechnology* 2008;19:305706. doi:10.1088/0957-4484/19/30/305706.