Effective in-field thermal conductivity of ferrofluids

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(Received 24 October 2017; accepted 11 December 2017; published online 24 January 2018)

A structural model to predict in-field thermal conductivity of ferrofluids is proposed in this study and is validated by the experimental data from the literature. The model is able to capture the aggregation development of the magnetic particles with increasing magnetic field strength. Introducing a compression function that can be found empirically, the model can accurately predict the thermal conductivity, especially the plateauing at low and high magnetic fields. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5010275>

I. INTRODUCTION

Magnetic fluids, generally referred to suspensions of micron-sized magnetic particles in a carrier liquid, were initially conceived in response to the need for a fluid with high magnetization properties.¹ With the progress in nanotechnology, the production of stable ferrofluids, colloidal dispersion of nano-sized magnets with a narrower size distribution in a carrier liquid, has been made possible. Ferrofluids are considered a subclass of nanofluids where there is a restriction on the particle size in nano range, usually about 10 nm, but no restrictions on the suspension's carrier liquid or the type of dispersed magnetic particles.^{2,3} Although the terms magnetic fluids and ferrofluids have often been used interchangeably, the former is referred to the early invention of dispersions of micron-sized magnetic particles in a liquid, whereas the latter is often used in reference to nano-sized magnetic particles dispersed in a liquid. Other terms such as magnetorheological fluids, magnetic colloids, magnetizable fluids, and ferrocolloids have also appeared in the literature.

In response to external stimuli such as a magnetic field or an electric field the physical properties of ferrofluids, including thermophysical, rheological, and optical properties, can be altered or controlled.⁴ Controllability of properties opens promising applications of ferrofluids in a broad field of technical and biomedical applications such as sensors, actuators, rotating or linear electrical drives, fine positioning systems, lubricated systems, adaptive bearing and dampers, micromechanical sensors, nondestructive defect sensors, magneto optical wavelength filters, optical switches, biosensors, diagnosis, hyperthermia treatment and tumor treatment, cell separation, and others.^{5–9}

Ferrofluids possess large magnetization in the presence of a magnetic field while retaining their fluid properties.¹⁰ Moreover, interactions between magnetic nanoparticles when coupled to the applied magnetic field lead to the formation of heterogeneous ordered structures along the field.¹¹ Due to the formation of field-assisted microstructures, effective thermal conductivity of the medium changes while certain thermodynamic properties such as effective heat capacity remain unaffected.¹² Early studies on thermophysical properties of

magnetic fluids did not present magnetic field dependency of ferrofluids' thermal conductivity,¹³ focusing primarily on investigations of heat transfer in ferrofluids by thermodiffusion and magnetoconvection or thermomagnetic convection phenomena.^{14,15}

An enhanced thermal conductivity of in-field ferrofluids, when temperature and magnetic field gradients are parallel, was later demonstrated by investigators through multiple experimental studies. In case of perpendicular orientation of the magnetic field with respect to the temperature gradient, no change or relatively small increase in thermal conductivity was observed.^{16,17} The phenomenon is consistent with the observations that magnetic particles form chain-like structures along the orientation of the magnetic field, but there is no such chain formation along the temperature gradient that is perpendicular to the magnetic field for this case.

Although many available experimental results in the literature do not show consistency in the degree of thermal conductivity enhancement, they lend support to the hypothesis that the particles' alignment in the field direction is primarily responsible for enhancing thermal conductivity.^{16–18}

Knowing that the formation of the microstructures is responsible for the thermal conductivity enhancement of in-field ferrofluids, an appropriate model that captures aggregation development of the particles would be the key element in predicting thermal conductivity. In an attempt to theoretically model in-field thermal conductivity of ferrofluid, models for the anisotropic feature of the medium owing to the formation of the chains were proposed.^{17,19–21} These models are similar to the anisotropic models for studying solid anisotropic composite materials.

A gas-like compression model to calculate the relationship between aggregation and magnetization of an in-field ferrofluid was proposed in the literature.²² This compression model introduced a hyperbolic tangent behavior (discussed subsequently below) and a compression parameter to account for particle–aggregate–fluid interactions. In the present study, a modified aggregation compression function is proposed, in conjunction with the findings of our previous study¹¹ that offered insights into the formation and growth of the field-induced microstructures. Then, a structural model

for an in-field ferrofluid as a heterogeneous medium is employed to develop a semi-empirical model to predict thermal conductivity of the anisotropic ferrofluid. The calculated values using the proposed model are compared with the available experimental data to show their acceptable agreement.

II. MORPHOLOGY OF THE FIELD-ASSISTED MICROSTRUCTURES

It has been both theoretically and experimentally shown that the magnetic nanoparticles in ferrofluid form microstructures in response to an external magnetic field. The process of assembling particles is influenced by both magnetic interactions and the matrix fluid rheology.^{23,24} On the magnetic interactions level, particle–particle interactions as well as particle–field interactions are primarily responsible for the formation of the short chains. The short chains undergo further interactions in stronger magnetic fields resulting in the growth of the microstructures. On the rheological side, the balance between the yield stress of the matrix fluid and interparticle magnetic stress controls the formation of the structures.²⁵

The influence of the external field on the aggregation behavior of the particles can be included in intensification of the interaction between the particles. It induces the formation of the assemblies from particles even with small dipole moments, as well as allowing the smaller aggregates to make longer or thicker chains in the zippering process.¹¹

The relative strengths of the dipolar interactions and coupling to the magnetic field with thermal energy are characterized by the coupling constant coefficient and the Langevin parameter α . The dimensionless coupling constant coefficient taking into account the steric layer of the magnetic particles is $\lambda^* = (d_m/d_p)^3 (\mu_0 M_d^2 V_p) / (24 k_B T)$ which compares the strength of the dipolar energy of the two particle in contact with the thermal energy $2k_B T$. Here, d_m (m) and d_p (m) are the magnetic core diameter and particle diameter, respectively, including the steric layer, $\mu_0 = 4\pi \times 10^{-7}$ (N/A²) is the permeability of free space, M_d (A/m) is the spontaneous magnetization of the solid particles, V_p (m³) is the volume of a single particle, T (K) is the temperature, and

$k_B = 1.381 \times 10^{-23}$ (J/K) is the Boltzmann's constant. Self-assembly of the particles starts at about $\lambda^* > 0.4$ for a typical ferrofluid containing magnetite particles of 10 nm.²⁶

Furthermore, the dipolar energy between the two particles which depends on magnetic moment of the particles (material properties and particle size) decays with the distance between the particles $\langle s \rangle^{-3}$ that is related to the volume fraction of the particle ϕ as²⁷

$$\langle s \rangle = \frac{d_p}{2} \left[\left(\frac{\phi_{hcp}}{\phi} \right)^{1/3} - 1 \right], \quad (1)$$

where $\phi_{hcp} = 0.74$ is a number corresponding to hexagonal close-packing spatial arrangement of particles.

Langevin parameter $\alpha = (mH)/(k_B T)$, known also as energy ratio, characterizes the particle–field interaction where $m = \mu_0 M_d V_p$ is the magnetic moment of the particles, and H (A/m) is magnetic field strength. The particles assembly in response to the external field starts when $\alpha > 1$. It has been also observed that in a weakly dipolar system where formation of the zero-field structures is scarce, even small particle–particle interactions can have large effects in a strong magnetic field.¹¹

The assembly of the particles with increasing magnetic field has been studied through a direct observation of the cryo-TEM images of the samples in the magnetic field. Figure 1 illustrates the process of assembling particles in an aqueous weak dipolar ferrofluid. The sample is homogeneous in the absence of a magnetic field. However, it responds to a relatively weak magnetic field of 51.5 mT resulting in the formation of the short chains. Once formed under the influence of an external magnetic field, the short chains undergo further aggregations processes in the stronger magnetic fields. If the chains are aligned with their dipole moments along the same line, these interactions are always attractive and result in further increase in the chain length due to head-to-tail aggregation. However, if the two chains interact with one another in a lateral direction, these interactions can be either attractive or repulsive. When the lateral interactions cause coalescence of the chains resulting in hexagonally packed bundles, the transition is known as zippering of the chains. More details are found in Ref. 11.

FIG. 1. Cryo-TEM observations of aqueous ferrofluid with magnetite nanoparticles of 10 nm, 0.5% (w/v%) concentration. From left to right: zero field, 200 (mT), and 370 (mT). The samples were prepared on holey carbon coated copper TEM grids (Quantifoil R2/2-Cu). The images show the process of assembling particles into chains and their growth with increasing magnetic field strength.

III. MODEL FOR EFFECTIVE THERMAL CONDUCTIVITY

Comprehensive investigations showed a moderate enhancement in the thermal conductivity of stable and isotropic nanofluids in comparison with their carrier liquid,^{28,29} consistent with the prediction by classical models such as the Maxwell model,³⁰ Hamilton-Crosser model,³¹ and effective medium theory model.³² Therefore, the isotropic thermal conductivity of ferrofluids in the absence of magnetic fields can be predicted by classical models. However, ferrofluids become strongly anisotropic in the presence of an externally applied field due to the formation of field-assisted assemblies.

The inset (a) in Fig. 2 illustrates the gradual change of a homogeneous medium in zero field to a heterogeneous ferrofluid with the field strengthening. The process of assembling particles progresses as the magnetic field increases. However, the development of the aggregation process depends on not only the magnetic field strength, but also the other factors including the rheological properties of the carrier liquid.

When a ferrofluid with volume fraction of ϕ in the total volume of V is exposed to a magnetic field, parallel assemblies in the field direction form aggregates that are separated from the surrounding dilute dispersion of the particles. As a result, the two structures can be found in the medium: the aggregates (Structure 1) that occupy volume V_{s1} with volume fraction of ϕ_{s1} , and the uniform dispersion of individual particles, dimers or trimers similar to what can be found in zero-field (Structure 2) that occupies the volume of V_{s2} with volume fraction of ϕ_{s2} .

Considering anisotropic nature of the in-field ferrofluid conductive heat transfers in the two principle directions of x ($\Delta T \parallel H$), and y ($\Delta T \perp H$) with appropriate equations are

expressed. Subsequently, a function that can appropriately demonstrate the aggregation behavior of the nanoparticles is proposed. Once an aggregation function is defined, directional effective thermal conductivities of the medium, $k_{eff,x}$ and $k_{eff,y}$, can be expressed with the contribution from the two structures as the weighted mean between the two.³³

A. Effective thermal conductivity parallel to magnetic field ($\Delta T \parallel H$)

If x is the direction of the applied magnetic field, and temperature gradient is parallel to it, particles will align themselves in the field direction in the form of parallel chains with the gap in between the chains filled by the fluid. As seen in the inset (b) of Fig. 2, the two parallel paths for total heat transfer through Structure 1, $q_{s1,x}$, are considered (1) heat transfer through the magnetic particles assuming their assemblies as parallel rods of solid, and (2) heat transfer through the fluid. Then, the total heat conduction q_x can be obtained as the sum of the heat transfers from Structure 1, $q_{s1,x}$, and Structure 2, q_2 . Applying the Fourier's law, it can be written as

$$q_x = k_{eff,x} \Delta A \frac{\Delta T}{\Delta x} = q_{s1,x} + q_{s2}, \quad (2)$$

$$q_{s1,x} = \frac{\Delta T}{R_{eq}} = k_{1,x} \Delta A_{s1} \frac{\Delta T}{\Delta x}, \quad (3)$$

$$q_{s2} = k_2 \Delta A_{s2} \frac{\Delta T}{\Delta x}, \quad (4)$$

where $k_{1,x}$ and k_2 are thermal conductivities of Structure 1 in the x -direction and the homogeneous dispersion, respectively.

FIG. 2. Schematic of a ferrofluid in the presence of an external magnetic field. (a) Transition of the medium from a homogeneous dispersion of magnetic nanoparticles in the absence of a field, where dimers or trimers can be seen at places, to a heterogeneous medium in the field, where aggregates are formed and grow. Two distinct structures in the heterogeneous ferrofluid can be seen: Structure 1 (aggregates separated from the carrier liquid), and Structure 2 (uniform dispersion) (b) parallel to the field direction, effective thermal conductivity is obtained by weighted mean of the conductivities of the two structures i.e., chains in parallel ordering with the fluid, and the uniform dispersion (c) perpendicular to the field direction, effective thermal conductivity is obtained by weighted mean of the conductivities of the two structures i.e., chains in series ordering with the fluid, and the uniform dispersion.

R_{eq} , the equivalent thermal resistance, has the general form of $R = l/(kA)$ and can be expressed for the two parallel paths as

$$\frac{1}{R_{eq,parallel}} = \frac{1}{R_{chains}} + \frac{1}{R_{fluid}} \quad (5)$$

or

$$\frac{1}{\frac{\Delta x}{k_{1,x} \cdot (\Delta y \cdot 1)}} = \frac{1}{\frac{\Delta x}{k_p \cdot (\Delta y_1 \cdot 1)}} + \frac{1}{\frac{\Delta x}{k_f \cdot (\Delta y_2 \cdot 1)}}, \quad (6)$$

$$k_{1,x} = k_p \frac{(\Delta y_1 \cdot 1) \cdot \Delta x}{(\Delta y \cdot 1) \cdot \Delta x} + k_f \frac{(\Delta y_2 \cdot 1) \cdot \Delta x}{(\Delta y \cdot 1) \cdot \Delta x}. \quad (7)$$

Assuming that the resistance for chains of particles is replaced by the resistance of an equivalent solid rod of the same total solid volume, and simplifying, the thermal conductivity of Structure 1 is obtained as follows:

$$k_{1,x} = k_p \frac{V_{p,s1}}{V_{s1}} + k_f \frac{V_{f,s1}}{V_{s1}}, \quad (8)$$

$$k_{1,x} = k_p \phi_{s1} + k_f (1 - \phi_{s1}), \quad (9)$$

where k_p and k_f are the thermal conductivities of the magnetic particles and the fluid, respectively.

As shown schematically in Fig. 2, Structure 2 is isotropic whose thermal conductivity k_2 can be obtained by employing the Maxwell model for a homogeneous colloid³⁰

$$k_2 = k_f \frac{k_p + 2k_f + 2\phi_{s2}(k_p - k_f)}{k_p + 2k_f - \phi_{s2}(k_p - k_f)}. \quad (10)$$

Having thermal conductivities of the two structures, the effective thermal conductivity in the field direction, x , can be found by weighted mean of the thermal conductivities of the two structures, $k_{1,x}$ and k_2 ³³

$$k_{eff,x} = f k_{1,x} + (1 - f) k_2, \quad (11)$$

where f is weighting parameter denoting fraction of the total volume of V that is occupied by the volume of Structure 1, V_{s1}

$$f = \frac{V_{s1}}{V}. \quad (12)$$

B. Effective thermal conductivity perpendicular to the magnetic field ($\Delta T \perp H$)

If the temperature gradient and magnetic field are perpendicularly oriented, with the selection of ΔT in the y direction and H in the x direction, heat transfer through Structure 1 in the y direction has two paths in series as seen in the inset (c) of Fig. 2. The total heat conduction q_y is the sum of the heat transfers from Structure 1, $q_{s1,y}$, and Structure 2, q_2 that can be obtained by applying the Fourier's law

$$q_y = k_{eff,y} \Delta A \frac{\Delta T}{\Delta y} = q_{s1,y} + q_2, \quad (13)$$

$$q_{s1,y} = \frac{\Delta T}{R_{eq}} = k_{1,y} \Delta A_{s1,y} \frac{\Delta T}{\Delta y}, \quad (14)$$

$$q_{s2} = k_2 \Delta A_{s2,y} \frac{\Delta T}{\Delta y}, \quad (15)$$

where $k_{1,y}$ and k_2 are thermal conductivities of Structure 1 in the y -direction and the homogeneous dispersion, respectively. R_{eq} , the equivalent thermal resistance for the two series paths, $R_{eq,series} = R_{chains} + R_{fluid}$, can be written as

$$\frac{\Delta y}{k_{1,y} \cdot (\Delta x \cdot 1)} = \frac{\Delta y_1}{k_p \cdot (\Delta x \cdot 1)} + \frac{\Delta y_2}{k_f \cdot (\Delta x \cdot 1)}, \quad (16)$$

$$k_{1,y} = \left(\frac{1}{k_p} \cdot \frac{\Delta y_1 \cdot (\Delta x \cdot 1)}{\Delta y \cdot (\Delta x \cdot 1)} + \frac{1}{k_f} \cdot \frac{\Delta y_2 \cdot (\Delta x \cdot 1)}{\Delta y \cdot (\Delta x \cdot 1)} \right)^{-1}. \quad (17)$$

As before, after simplifying, the effective thermal conductivity of Structure 1 is obtained

$$k_{1,y} = \left(\frac{1}{k_p} \cdot \frac{V_{p,s1}}{V_{s1}} + \frac{1}{k_f} \cdot \frac{V_{f,s1}}{V_{s1}} \right)^{-1}, \quad (18)$$

$$k_{1,y} = \left(\frac{\phi_{s1}}{k_p} + \frac{1 - \phi_{s1}}{k_f} \right)^{-1}. \quad (19)$$

Since Structure 2 is isotropic, the thermal conductivity is not directional and can be obtained from the Maxwell model given in Eq. (10). The weighted mean of thermal conductivities of the two structures will give the effective thermal conductivity of the ferrofluid in the direction of temperature gradient as

$$k_{eff,y} = f k_{1,y} + (1 - f) k_2. \quad (20)$$

In order to solve Eqs. (11) and (20), one should define f , weighted parameter, for which an expression for the volume fractions of the structures is required.

C. Volume fraction of structure 1: Parallel microstructures

As described in Sec. II, the growth of the aggregates depends on the relative strengths of the dipolar interactions or coupling to the magnetic field compared with thermal energy, as well as the balance between the interparticle magnetic stress and the matrix fluid yield stress which are, respectively, characterized by the coupling constant λ^* , the energy ratio α , and the dimensionless yield parameter, $Y_{M,\phi}^*$, is the characteristic interparticle magnetic stress compared with the matrix fluid yield stress. Therefore, the volume of Structure 1, V_{s1} , that is, the volume occupied by aggregates, can be defined as

$$\phi_{s1}(\lambda^*, \alpha, Y_{M,\phi}^*) = \frac{N_1 V_p}{V_{s1}}, \quad (21)$$

where N_1 and V_{s1} are the number of particles that contributes to the chaining process and the volume of the aggregates, respectively.

To model ϕ_{s1} , the development made by Li *et al.*²² is considered. Using the analysis that followed a model of gas-like compression, the aggregation of magnetic nanoparticles is shown to be best approximated by a hyperbolic tangent.

Without loss of generality, the hyperbolic tangent function can be used to model the chain formation in Structure 1 as

$$\varphi_{s1} = A \tanh(\xi \alpha^2) + B, \quad (22)$$

where A and B are constants and ξ is a compression function which describes the process of the particles aggregation in ferrofluid when a magnetic field is applied. Its definition will be discussed in Sec. III E.

In the absence of a magnetic field ($\alpha = 0$), the distribution of the particles in Structure 1 has a uniform pattern similar to the original sample, that is, $\varphi_{s1} = \varphi$, where φ , assuming that there exist N number of identical spherical particles with volume of V_p suspended in a total volume of V , can be written as

$$\varphi = \frac{NV_p}{V}. \quad (23)$$

As α increases, φ_{s1} nonlinearly increases until at a high field ($\alpha \rightarrow \infty$) all the particles contribute to the chaining process giving the maximum attainable concentration $\varphi_{s1} = 0.74$. The arrangement of the magnetic particles in high magnetic fields has been shown as a hexagonal close-packing spatial arrangement with the corresponding volume concentration of 0.74.³⁴ The system will reach the maximum volume fraction of 0.74 if the particles are close enough to interact with each other, and the magnetic force within the ferrofluid is strong enough to dominate over the yield stress of the matrix fluid allowing the particles and the aggregates to undergo further assembly processes. Equation (22) becomes

$$\varphi_{s1} = (0.74 - \varphi) \tanh(\xi \alpha^2) + \varphi. \quad (24)$$

The volume of Structure 1 also changes in accordance with the growth of the chains. Considering a fixed number of particles in a representative volume of Structure 1, the volume V_{s1} will vary in the same manner as φ_{s1} , the solid volume fraction. Thus, an expression for V_{s1} can be thought as

$$V_{s1} = C \tanh(\xi \alpha^2) + D, \quad (25)$$

where C and D are constants. Equation (25) must satisfy the following conditions:

$$\begin{aligned} (1) \quad (\alpha = 0) &\rightarrow V_{s1} = 0, \\ (2) \quad (\alpha \rightarrow \infty) &\rightarrow V_{s1} = \frac{\varphi}{0.74} V. \end{aligned} \quad (26)$$

Physically the above represent the two extreme cases of zero field and very high field, respectively. At zero field, Structure 1 is absent, and thus, its volume is zero. At a very high field strength, all the particles are in Structure 1 in a hexagonal close-packing configuration. Applying Eq. (26) into Eq. (25), an expression for the change in the volume of Structure 1 can be obtained

$$V_{s1} = \frac{\varphi}{0.74} V \tanh(\xi \alpha^2). \quad (27)$$

The dimensionless parameter f is defined as the weighting parameter which is the ratio of volume of Structure 1 that is occupied by chains, to the total volume. That is

$$f = \frac{V_{s1}}{V} = \frac{\varphi}{0.74} \tanh(\xi \alpha^2). \quad (28)$$

D. Volume fraction of structure 2: Uniform dispersion

The process of the increase in the volume fraction of Structure 1 is equivalent to the decrease in the volume fraction of Structure 2, which consists of a uniform dispersion of individual particles, dimers, or trimers at places. If the number of particles and the volume of Structure 2 are N_2 and V_{s2} , respectively, the volume fraction of Structure 2 can be written as

$$\varphi_{s2}(\alpha) = \frac{N_2 V_p}{V_{s2}}. \quad (29)$$

A simple algebraic calculation using Eqs. (23), (21), and (28) gives

$$\varphi_{s2} = \frac{(N - N_1) V_p}{V - V_{s1}} = \frac{\varphi V - f \varphi_{s1} V}{V - f V} = \frac{\varphi - f \varphi_{s1}}{1 - f}. \quad (30)$$

E. Compression function ξ

The compression function ξ in Eq. (22) has to be modeled or empirically determined in order to eventually ascertain thermal conductivity. In literature where a hyperbolic tangent function has been used to model nanoparticle response to magnetic fields, as in Eq. (22), a compression constant, independent of both α and φ , has been introduced, which is multiplied by either φ^2 or φ .^{21,22} The resultant expression was explained as a compressibility factor that describes the interaction behavior between particles in ferrofluid that is related to not only the dipolar coupling constant but also the treatment method for preventing particles aggregation such as surfactant or charged particles. In this study, we introduce the compression function, ξ , and seek to relate it to not only the particle–particle interaction, but also characteristics of the nanoparticle–fluid combination.

It is known that the behavior of the suspended magnetic particles is influenced by the matrix fluid rheology, which is typically Newtonian. The ability of the matrix fluid yield stress to freeze structures in place along the Newtonian trajectory resulting in the growth of the chains to be arrested has been shown.²⁵ In a 3-dimensional system, the magnetic yield parameter $Y_{M,\varphi}^*$ that characterizes the balance between interparticle magnetic stress and the matrix fluid yield stress τ_y with incorporation of the concentration variations is found to appropriately govern the structure of such a system, that is

$$Y_{M,\varphi}^* = \frac{\mu_0 C (\rho M)^2}{12 \tau_y} \varphi^3, \quad (31)$$

where C is a constant that relates the matrix fluid yield stress to the critical force necessary to cause an embedded particle to yield, ρ is the particle mass density, and M , the particle magnetization per unit mass, is $m/(\rho V_p)$.

On the particle–particle level, the dipole–dipole interactions are distance dependent which scale with $\langle s \rangle^{-3}$ for

strongly correlated in-line dipoles, and $\langle s \rangle^{-6}$ for decoherent dipoles.^{11,26} Knowing that the average particle separation s scales with $\varphi^{-1/3}$ [Eq. (1)], the dipolar interaction scales with φ or φ^2 corresponding to the two scenarios.

To appropriately include the chaining process of the particles addressing both the particle–particle interactions, and rheology of the matrix fluid based on Eq. (21), ξ in Eq. (22) can be thought as

$$\xi = \sum_{j=1}^3 A_j \varphi^j, \quad (32)$$

where A_j are the constant coefficients reflecting the contribution from particle–particle and particle–fluid interactions, including the treatment method of the particles as well as the rheological behavior of the aggregates in the ferrofluid. The coefficients in Eq. (32) can be empirically determined.

F. Steps to compute thermal conductivity

To compute the thermal conductivity of ferrofluids in the presence of magnetic fields by using the present model, the following sequential steps are followed. Noting the magnetic field H and particle's size and material, the Langevin parameter α is computed. Assuming that the expression for the compression function ξ is known for the particle–fluid combination, the volume fraction φ_{s1} of ordered structures is computed, followed by weighting parameter f and volume fraction φ_{s2} of the remaining uniformly dispersed volume. Then, the thermal conductivities $k_{1,x}$, $k_{1,y}$, and k_2 are computed, as is the effective thermal conductivity, taking into account whether the magnetic field is parallel or perpendicular to the temperature gradient.

To find the expression for ξ , a small set of the obtained data can be used as a training set. The requirement is that multiple data points corresponding to three values of φ should be used. Since the inverse solution of finding the ξ value for a given value of conductivity is not obvious, an iterative scheme can be set up where an initial guess of ξ is made and subsequent iterations refine the value by attempting to bring the computed values of conductivities to match the measured ones.

IV. RESULTS AND DISCUSSION

To validate the proposed model, a set of experimental measurements of thermal conductivity of the kerosene-based ferrofluid with magnetite nanoparticles of about 9.8 nm using transient hot wire method from Ref. 18 has been used. The probe sensor of the instrument was found unaffected in the magnetic field within the range of 0–300 G (0–0.03 T). To find the compression expression, the compression values corresponding to each set of data for a specific concentration were found, from which the constants in Eq. (32) were determined.

Following the steps explained in Sec. III F, thermal conductivities are computed and plotted (see Fig. 3). As seen in Fig. 3, the experimental data are in a reasonable agreement with the theoretical predictions by the proposed model.

FIG. 3. Thermal conductivity enhancement as a function of magnetic field strength, experimental data (scattered data points) with 5% error bar, corresponding to the thermal conductivity measurements from the literature¹⁸ for the kerosene-based magnetite ferrofluids of 0.031%, 0.41%, 0.82%, and 1.71% (v/v%) containing particle size of 9.8 nm, compared with the theoretical prediction using the model proposed in this study (solid lines).

Similar procedures is followed to find the compression function for ferrofluids containing magnetite particles with an average size of 75 nm dispersed in ethylene glycol (EG) using the experimental set of data obtained by Katiar *et al.*³⁵ Multiple data points corresponding to three concentration values have been employed as the training set to find compression function ξ . Thermal conductivities are then computed and plotted for all different concentration values ranging from 1% to 7% as seen in Fig. 4. The predictions using the proposed model in this study show a better agreement with the experimental data than those of the theoretical model proposed in Ref. 35.

The plateauing of effective conductivity values at low and high magnetic fields is intuitively expected consistent with the chaining process that is initiated when the energy

FIG. 4. Thermal conductivity enhancement for ethylene glycol-based ferrofluids of different volume fractions (1%–7%) containing magnetite particles with an average size of 75 nm. The predictions from the proposed model in this study (solid lines) are in better agreement with the experimental data (filled circles with uncertainty bars, from the literature³⁵) than those from the proposed model in Ref. 35 (dashed lines).

ratio crosses the threshold value ($\alpha = 1$), and it ends when ferrofluid becomes saturated at a high magnetic field.¹² This trend is reflected in the experimental measurements^{18,35} and the model presented in this study is able to not only predict the flattening at low and high values of the field, but also accurately capture the increasing trend. This is due to the hyperbolic tangent modeling [Eqs. (24)–(28)] and the compression function ξ introduced in the present study. Previously proposed model that exhibited an asymptotic flattening at low and high fields had used a constant compression factor²¹ that gives a best fit to the particular experimental data, while the current model allows different compression functions for different particle–fluid combinations.

V. CONCLUSION

Considering the anisotropic feature of the ferrofluids due to the formation of ordered microstructures when subject to a magnetic field, a structural model has been developed to predict the in-field thermal conductivity of ferrofluids. The proposed model has taken into account the process of particles assembly which changes the distribution pattern of the particles from homogeneous dispersion medium to a non-uniform aggregated particle–liquid one. Because of the formation of the chains, the ferrofluid changes from an isotropic medium in which the properties are not directional to an anisotropic one. As the transition pattern of the aggregation depends on the particle–particle interaction, particle–field interaction, as well as on the rheology of the matrix fluid, a model that reflects the influence of the aforementioned factors on the aggregation behavior of the particles has been proposed.

The model is a semi-empirical model as it includes a compression function, ξ , which is concentration dependent and is to be found to be empirical. The empirically found function can appropriately address the contribution of the factors that are difficult to be analytically taken into account such as the treatment method of the particles, polydispersity, and rheology of the matrix fluid. The model has been employed to predict the thermal conductivities of the Fe_3O_4 -kerosene and Fe_3O_4 -ethylene glycol ferrofluids using the experimental data taken from the two independent references.^{18,35} The predictions have been found to be in a good agreement with experimental data showing that the proposed model can appropriately envisage the aggregation development and thereby the in-field thermal conductivity of ferrofluids.

Once the geometrical structure of the medium is known, the thermal conductivity model described in this paper is a structural model. It is therefore also applicable for predicting the anisotropic thermal conductivity of composite systems where two or more phases can be distinguished and the structural or geometrical distribution of the phases is known or is predictable. Further, the 2-D anisotropy considered in the present study can be extended to a 3-D anisotropy model.

ACKNOWLEDGMENTS

The cryo-TEM images collected at the New York Structural Biology Center (NYSBC) were made possible by

a Grant from NYSTAR. The investigation was conducted in a facility constructed with the support from the Research Facilities Improvement Program Grant No. C06 RR017528-01-CEM from the National Center for Research Resources, National Institutes of Health. The authors would like to thank NYSBC's staff of scientists for providing access to the cryo-TEM facilities. Special thanks to Dr. Mariena Silvestry Ramos for her helpful advice and comments on cryogenic-TEM imaging.

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