TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC SƯ PHẠM TP HỒ CHÍ MINH
Tập 20, Số 3 (2023): 458-467
Website: https://journal.hcmue.edu.vn
ISSN: 2734-9918

HO CHI MINH CITY UNIVERSITY OF EDUCATION
JOURNAL OF SCIENCE
Vol. 20, No. 3 (2023): 458-467
https://doi.org/10.54607/hcmue.js.20.3.3677(2023)

Research Article

PARTICLE SIZE -DEPENDENT MAGNETIC PROPERTIES OF NANOFLUIDS BASED ON MAGNETITE NANOPARTICLES: A COMPUTER SIMULATION STUDY

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Received: November 27, 2022; Revised: February 14, 2023; Accepted: March 16, 2023

ABSTRACT

Magnetic nanofluids are an outstanding candidate for biomedicine research. This is because their magnetic properties play a significant role in evaluating the effectiveness of clinical applications in biomedicine. Besides, that is influenced by many factors, the most important of which is particle size. In this article, we present a simulation study to assess the effect of particle size on the magnetic properties of magnetic fluids which contain the magnetite (Fe_3O_4*) nanoparticles ensemble with their physical size variation between 2 nm and 20 nm (Critical size range for biomedical applications). These results show that the magnetic properties of microfluidics strongly depend on the size of the component nanoparticles. In addition, they are also compared with experimental results reported by other authors recently, showing good agreement and providing some valuable predictions.*

Keywords: computer simulation; magnetic properties; nanofluids; particle size

1. Introduction

A few decades back, magnetic nanofluids gained increasing interdisciplinary scientific interest because of their fascinating properties and great potential in biomedical applications like a magnetic separation (Nithya et al., 2021), hyperthermia therapy (Gawali et al., 2021), and targeted drug delivery systems (TDDS) (Kianfar, 2021). They are a stable colloidal dispersion of various solid magnetic nanoparticles. Besides, magnetite (Fe_3O_4) nanoparticles (MNPs) have many advantages, such as low toxicity, biocompatibility, and being easily

Cite this article as: Nguyen Thanh Hoang, Nguyen Le Hoai Phuong, & Nguyen Manh Tuan (2023**)**. Particle size -dependent magnetic properties of nanofluids based on magnetite nanoparticles: A computer simulation study. *Ho Chi Minh City University of Education Journal of Science, 20*(3), 458-467.

embedded inside various biodegradable carriers. Therefore, these unique multifunctional properties make them one of the most common nanomaterials to form ferrofluids (FF).

As we know, evaluating the effectiveness of those biomedical applications must partly based on their physical properties (Kappiyoor et al., 2010) and is strongly dependent on the physical size of the MNPs inside the FF, especially on the nanometer scale (Andrievski & Glezer, 2001; Lue, 2007; Mason et al., 2007). Thence, investigating the size effect on their physical properties plays a significant role. Particle size affects many factors, such as thermal conductivity (Dadwal & Joy, 2020; Ganesan et al., 2018), specific power absorption in AC magnetic field (Ma et al., 2004), and rheological property (Wu et al., 2016). Besides, in the above biomedical applications, an external magnetic field is applied, and it becomes increasingly important to investigate the influence of particle size on magnetic properties. In the first step to perform an experimental investigation, the FF containing the MNPs ensemble is fabricated by common methods, such as co-precipitation, thermal decomposition, sol-gel process, solvothermal technique, polyol method, and microemulsion (Niculescu et al., 2021). The first one is the simplest and most widely used chemical method but still has some drawbacks in the broad particle size distribution of products.

Meanwhile, the last one can control the size of obtained nanoparticles but is complicated and requires an isotropic, macroscopically homogeneous, and thermodynamically stable solution containing a polar phase, a nonpolar phase, and a surfactant (Niculescu et al., 2021). Furthermore, synthetic samples must be characterized by some modern experimental protocols like Vibrating sample magnetometer (VSM) and superparamagnetic resonance (SPR) technique that allows obtaining results assessing the magnetic properties of the FF. Therefore, investigating the influence of the particle size on the magnetic properties of the FF by the experiment requires the repetition of these procedures many times. As a result, it has led to a waste of time and material resources. However, numerical and computer simulation methods can solve these issues. Köseoglu & Kavas investigated the FF by SPR technique and later applied a theoretical formalism based on a distribution diameter (Köseoglu & Kavas, 2008). Though the particle size is only in the range of 1.1-11 nm, sizes above 11 nm have not been investigated yet. In addition, the influence of the crystallite size of the MNPs system on their magnetic properties (in the range of 9-53 nm) by experimental studies has been reported by Upadhyay et al. (2016). This is just merely average crystallite size (the crystallite size is the physical size if and only if the particle is single-domain), which is based on the X-ray diffraction pattern (using Scherrer's formula) (Kril & Birringer, 1998). Here, the crystallite sizes of the MNPs below 9 nm and the physical particle sizes have not been discussed yet. The particle size below 20 nm (near the superparamagnetic region) is particularly important for the biomedical applications mentioned.

In this article, we present our computer simulation study based on an open-source package (VAMPIRE software) (Evans et al., 2014) to simulate an atomistic spin model for

the ensemble of randomly dispersed MNPs to represent the FF. There are always interparticle interactions among the MNPs inside the magnetic fluid, especially the dipolar interaction, which is often neglected due to computational complexity in some of the reported studies (Ludwig et al., 2013). The atomistic spin model simulation of magnetic nanomaterials supplies detail about the fundamental physical processes that govern their macroscopic properties and allows the simulation of complex effects like inter-particle interactions. Moreover, it is not only available to perform an atomistic spin model simulation for magnetic materials with different simulation methods like Monte Carlo integration (Gubernatis, 2005), Landau-Lifshitz-Gilbert (LLG) (Gilbert, 1955), Heisenberg mean-field theory (Paradezhenko et al., 2021) but also the accurate calculation of the dipolar interaction using two methods: macrocell approximation (Bowden et al., 2016) and tensor approach (Zhi et al., 2020), the latter is faster than the former. Previous studies have demonstrated that the LLG-Heun method is suitable for magnetic dynamic systems with evolution in time (Arjmand et al., 2018; García-Palacios & Lázaro, 1998). Thus, this work focuses on using the LLG-Heun method and the tensor approach to study hysteresis loop curves of the MNPs ensemble. Those allow investigation of the effect of particle size on their magnetic properties simply, effectively, and sparingly.

2. Materials and methods

2.1. Theoretical background and model

Here we describe the two major theories used in our computer simulation: the atomistic spin model and LLG integration.

Computer simulations were carried out using an atomistic spin model, which is the fundamental framework for VAMPIRE software working. The energy of the MNPs system is generally described in terms of the Hamiltonian H as the sum of all energy contributions. The four most significant contributors include the exchange interaction between pairs of local spins (H_{exc}), the magnetic uniaxial anisotropy (H_{ani}), the applied field (H_{app}), and the dipolar field (H_{dip}). Typical Heisenberg-type spin Hamiltonian employed in the calculations are given as follows:

$$H = H_{exc} + H_{ani} + H_{app} + H_{dip} \tag{1}$$

$$H = -\sum_{i \neq j} J_{ij} S_i . S_j - k_{eff} \sum_i (S_i . e)^2 - \sum_i \mu_s S_i . B + \frac{\mu_0 \mu_s}{4\pi r_{ij}^3} \left[S_i . S_i - \frac{3}{r_{ij}^{\ 3}} (S_i . r_{ij})(S_j . r_{ij}) \right] \tag{2}$$

Where J_{ij} describes the contributions of the exchange interaction between the magnetic moments i and j of the nearest neighbors, the S_i and S_j are unit vectors denoting the local spin moment direction. Besides, k_{eff} is the effective anisotropy energy per atom, $k_{eff}=K_{eff}.a^3/n_{at}$ with K_{eff} is the effective anisotropy energy, a is the system size, and n_{at} is the number of atoms. Meanwhile, μ_s is the atomic magnetic moment, and B is the applied

magnetic field. Finally, r_{ij} is the distance between spin i and j, μ_0 is the vacuum permeability, and μ_s is the local spin moment.

The Hamiltonian can describe the energy of the MNPs system but does not give information about the dynamics of the spin. To tackle this issue, the atomistic LLG equation is used to govern the dynamic behavior of the spin and is given by:

$$\frac{\partial S_i}{\partial t} = -\frac{\gamma}{(1+\lambda^2)}\left[S_i \times H_{eff}^i + \lambda S_i \times \left(S_i \times H_{eff}^i\right)\right] \quad (3)$$

Where λ is the phenomenological damping parameter (Gilbert damping parameter - an intrinsic property of the magnetic material). Meanwhile, γ is the gyromagnetic ratio, and H^i_{eff} is the net effective magnetic field on each spin. The H^i_{eff} is given by:

$$H_{eff}^i = -\frac{1}{\mu_z}\frac{\partial H}{\partial S_i} + H_{th}^i \quad (4)$$

The thermal fluctuations are represented by a Gaussian distribution in three dimensions with a mean of zero. At each time step, the instantaneous thermal field on each spin i is given by:

$$H_{th}^i = \Gamma(t)\sqrt{\frac{2\lambda k_B T}{\gamma \mu_s \Delta t}} \quad (5)$$

Where k_B is the Boltzmann constant, T is the system temperature, and Δt is the integration time step.

The LLG equation is integrated numerically using the Heun numerical scheme, which becomes the LLG-Heun method (García-Palacios & Lázaro, 1998), available in VAMPIRE software. It is a feasible method of integration to simulate the evolution of spin dynamics. That allows the implementation of the magnetization curve simulations of the MNPs.

2.2. Computer simulations

The magnetic fluid contains a random matrix of the spherical-like MNPs generated (system size is 200 nm × 200 nm × 200 nm). The effective anisotropy constant K_{eff} = 15 (kJ/m^3) (Mamiya et al., 2020), and the λ value was taken equal to 1.0 for all simulations. The simulation hysteresis loops at room temperature (300K) with particle size was changed (in the range of 2-20 nm) to investigate the effect of particle size on their magnetic properties. Besides, it is important to note that the magnetization data were presented as normalized magnetization ($m=M/M_s$). Where M_s is the saturation magnetization and M is the magnetization of the MNPs ensemble, respectively. The purpose of this is to compare the results obtained from the simulation with experimental results from other scholars. The computer simulations in this work were performed simultaneously on different nodes to save time. Besides, each job is done using parallel computing architectures (based on Message

Passing Interface - MPI) on two nodes (20 cores per node) to accelerate computational simulations.

3. Results and discussion

The simulation hysteresis loops for the MNPs ensembles with different particle sizes are shown in Figure 1. They show differences in shape and obtained magnetic parameters, namely, saturation magnetization, remanent magnetization, and coercive field. In the case of small particle size (2 nm) (Figure 2a, b), the magnetization curve has no hysteresis contemporaneous the magnetization becomes linear to the applied magnetic field. In addition, thermal noise influence on switching dynamic of magnetic moments (Berkov, 2002). The cause is due to the relaxation time being so small that several flips may occur during the time it takes to measure or simulate the magnetization (Aharoni, 1992). The increasing particle size has led to an increasing amount of magnetic moment of the MNPs. Therefore, the orientation of the magnetic moments is not coherent (Figure 2c). As a result, the appearance of hysteresis has led to the magnetization no longer being linear to the applied field.

The more specific assess shown in Figure 2d, e. Moreover, the magnetic values data are fitted by a suitable function to try to suggest a correlation between the particle size of the MNPs and their magnetic properties. As the raising of particle size, the saturation magnetization value (M_s) increased sharply (from 2 nm to 5 nm), then continued to increase almost linearly which respect to the particle size (Figure 2d). In addition, the change in remanent magnetization value (M_r) is generally increasing (Figure 2e) to the Log-normal function. Last but most important, the coercive field (H_c) increases with the increases of the particle size in the investigated range (2 - 20 nm) (Figure 2d). The highly H_c value may be caused by the strong spin interactions in highly crystalline during spin alignment, so larger particles need larger field energies against the magnetization (Li et al., 2017).

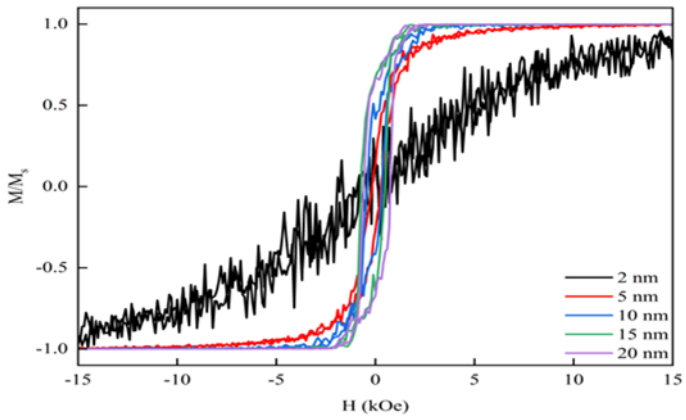

Figure 1. *The simulation hysteresis loops of the MNP ensembles*

with different particle size

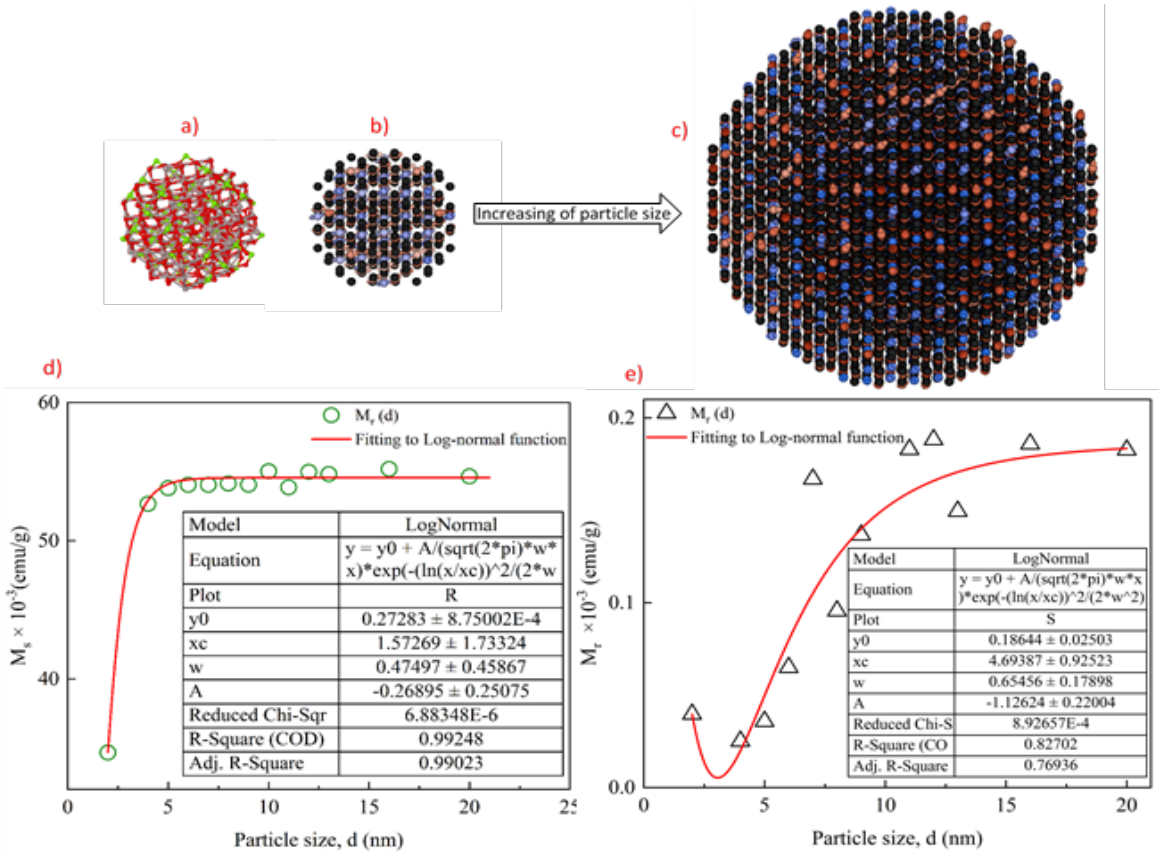

Figure 2. *Particle size dependence of magnetic properties of the MNPs ensemble: a) Crystalline structure of a* Fe_3O_4 *nanoparticle. b, c) A snapshot of spin configuration in the hysteresis loop magnetization simulations. d) Saturation magnetization; e) Remanent magnetization*

To investigate more clearly the correlation between the coercive field value H_c and the particle size, a Log-normal distribution function to fitting the H_c values (Figure 3) was used, which consists of our simulation results (the blue open square) and the experimental result reported by Li et al. (the red star) for spherical MNPs (Li et al., 2017), shown by the solid red line (Figure 3). That gives a good agreement between the experimental and simulation results. Based on this result, it can be perceived that the particle sizes for the maximum H_c value were determined to be about 90 ± 2 nm. Following Li et al., this value is a critical size for the transition from single-domain to multi-domain, which is 76 nm for cube-like Fe_3O_4 particles, that lower than the above value for the sphere-like particle (~90 nm). Though Li et al. also discussed the difference in H_c values between them and explained that the main reason is polycrystalline has multiple orientations in the sphere-like MNPs, which is considered to be the reason for their lower H_c values compared with those of the cube-like MNPs. However, the difference in critical size values between these two types of particle morphology has not yet been mentioned and discussed. We speculate that the cause may be

the influence of the MNPs' surface geometry on the FF's magnetic properties. Herein, further studies from others are still necessary to investigate. Much work remains to do.

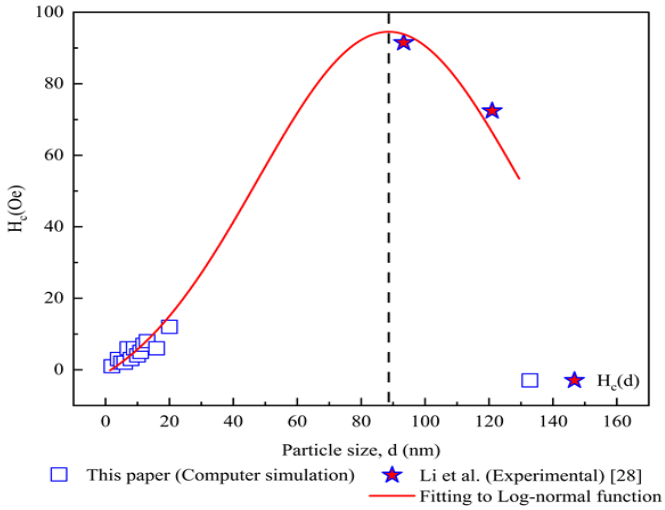

Figure 3. *Particle size dependence of the coercive field (H_c).*
The red star was replotted by refs (Li et al., 2017)

4. Conclusions

Particle size plays a significant role in determining the physical properties in general and magnetic properties in particular of magnetic fluids. In this work, computer simulation was applied to simulate the magnetic dynamic behavior, which includes the complex magnetic inter-particle interactions among the nanoparticles. Simulating and investigating the hysteresis loop magnetization curves of the MNPs ensemble, we have provided a simple method to clarify the strong influence of particle size on the magnetic properties of the FF. The correlation between the magnetic properties and the particle size concerning the log-normal function was also presented, which allows the prediction of the critical size and the other magnetic parameters based on the particle size. In addition, the study also shows partly the effects of different shapes on the magnetic properties of magnetic fluids, which could form a rewarding prediction for our further studies. In summary, changing the particle size will also lead to a change in the magnetic properties of the FF, indirectly affecting the effectiveness of biomedical applications.

❖ ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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TÍNH CHẤT TỪ PHỤ THUỘC KÍCH THƯỚC HẠT CỦA VI LỎNG NANO SẮT TỪ: MỘT NGHIÊN CỨU MÔ PHỎNG MÁY TÍNH

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Ngày nhận bài: 27-11-2022; ngày nhận bài sửa: 14-02-2023; ngày duyệt đăng: 16-3-2023

TÓM TẮT

Vài thập kỉ trở lại đây, vi lỏng nano từ tính là một ứng cử viên tiềm năng cho nghiên cứu y sinh học. Tính chất từ tính của chúng đóng vai trò quan trọng trong việc đánh giá hiệu quả của các ứng dụng lâm sàng trong y sinh học. Nó bị ảnh hưởng bởi nhiều yếu tố, trong đó quan trọng nhất là kích thước hạt. Trong bài báo này, chúng tôi trình bày một nghiên cứu mô phỏng máy tính nhằm đánh giá ảnh hưởng của kích thước hạt đến tính chất từ của vi lỏng chứa tổ hợp các hạt nano sắt từ (Fe_3O_4*) với sự thay đổi kích thước vật lí của chúng trong khoảng từ 2 nm đến 20 nm (Khoảng kích thước quan trọng cho các ứng dụng y sinh học). Các kết quả thu được cho thấy tính chất từ của vi lỏng phụ thuộc mạnh mẽ vào kích thước của các hạt nano thành phần. Ngoài ra, kết quả mô phỏng cũng được tham chiếu với các kết quả thu được từ thực nghiệm được báo cáo bởi các tác giả khác trong thời gian gần đây, cho thấy sự phù hợp tốt và đưa ra một số tiên nghiệm có giá trị nhất định.*

Từ khóa: mô phỏng máy tính; tính chất từ; vi lỏng nano; kích thước hạt