Thermal behaviour and particle size evaluation of primary clusters in a water-based magnetic fluid

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Abstract

This paper reports the experimental research on thermal behaviour and particle size evaluation of primary clusters of ferromagnetic nanoparticles in a water-based magnetic fluid. The magnetic fluids are suspensions of ultra fine particles coated with a molecular layer of dispersant in a liquid carrier such as water or kerosene. The particles are coated with single- or double-layer of surfactant to achieve stable dispersion. Numerous experimental studies have indicated the existence of the primary cluster of ferromagnetic nano-particles in a water-based magnetic fluid. The purpose of this research is to evaluate the particle size of the primary clusters by applying the Einstein’s equation for Brownian motion assuming that the primary cluster has a spherical-shape. The thermal behaviour of ferromagnetic nano-particles in magnetic fluids is investigated through the micro visualization using the optical darkfield microscope system and particle tracking velocimetry data processing system. Real-time visualization of the Brownian motion of primary clusters in a water-based magnetic fluid was carried out. The experimental results clarified that the primary cluster size depends upon the concentration of the ferromagnetic nano-particle in the magnetic fluid.

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1. Introduction

Recently, with the development of the micro electro-mechanical system technology and nano-technology, significant progress has been made in the field of microfluidic device flow or micro channel flow. In this respect, the interests in the application of the magnetic fluids to control the micro-channel flow have been increasing. This has been one of the prominent topics in nano-technology. By applying the magnetic fluid as a tracer particle in the micro-channel flow, feasibility to control the flow field using a magnetic field is investigated.

The magnetic fluids contain solid, magnetic, single domain particles coated with a molecular layer of a dispersant in a liquid carrier such as water or kerosene. Since the diameter of these particles lies in the size range of 5–15 nm, and due to the thermal agitation, the resulting random walk and random rotation, i.e. Brownian motion, the ferromagnetic nano-particles remain suspended steadily. To achieve a stable dispersion in non-polar or polar solvent, the particles are coated with a single or double layers surfactant.

Many experimental studies have suggested that when a magnetic-field is applied to a magnetic fluid, some of the ferromagnetic particles would form chain-like clusters [1]. Kamiyama and Satoh [2] investigated the effect of a magnetic-field on apparent viscosity of a magnetic fluid caused by clustering. They found that cluster formation is particularly conspicuous in the case of water-based magnetic fluid. Nakatani [3] and Jayadevan and Nakatani [4] found that in the water-based magnetic fluid large numbers of agglomerated magnetic particles are observed even in zero external fields using a darkfield observation.
system. They pointed out that much larger value of apparent viscosity in the water-based magnetic fluid is caused by this agglomerated magnetic particles. They also assumed that the agglomerated magnetic particles are of non-spherical shape, which is most probably considered a circle- or disk-shape in the size of about 200 nm diameter. Nakatani identified this agglomeration as primary cluster.

However, there are relatively few studies that specifically addressed the evaluation of the primary clusters’ size. Hence, it is indispensable to identify the size of primary cluster for micro-channel control using magnetic fluid. Several techniques such as flow cytometry, phase Doppler anemometry, electrostatics and optical tweezers are available for measuring the light scattering characteristics and size evaluation of individual particles. However, the measurable particle size is still limited in the range of 1–10 μm.

In the present study, thermal behaviour of ferromagnetic nano-particles in a water-based magnetic fluid was investigated using an optical microscope system. Real-time observation of the Brownian motion of ferromagnetic nanoparticles was effectively carried out using the darkfield condenser lens system. The Brownian motion of ferromagnetic nano-particles was analyzed by means of the particle tracking velocimetry (PTV) to obtain the velocity field. Assuming the primary cluster as spherical shape and using the velocity value of the particle motion and Einstein’s equation for Brownian motion, the particle size of the primary cluster of ferromagnetic nano-particles in a water-based magnetic fluid was obtained. The influence of the concentration of magnetic particle in a magnetic fluid on particle size evaluation was also investigated.

2. Experimental setup

The original magnetic fluid is water-based magnetic fluid W-40 (made by Taiho Industries Co. Ltd) with 40% weight concentration of fine magnetite particles (Fe₃O₄) in a water carrier, having a dynamic viscosity and density of 15.7 mPa s and 1.38 g/cm³ at 23 °C, respectively. In the present experiment, the tested magnetic fluid is diluted with pure water to change the density and viscosity of the fluid. Fig. 1 shows the distribution of density and dynamic viscosity as a function of weight concentration of ferromagnetic nano-particles in a water-based magnetic fluid.

Considering that optical microscopes have diffraction-limited resolutions approaching 500 nm in the lateral directions, the light scattered by nano-size particles were observed using the darkfield microscope system with oil immersion darkfield condenser lens made by Olympus U-DCW. In order to attain reliable observation, a high quality microscope designed with high numerical aperture, low field curvature, low distortion, and corrected for spherical and chromatic aberrations is required. For this purpose, the universal plan Apochromat lens (Olympus UPLAPO 100XOI3PH) was selected for the microscope system (Olympus BX50) using 12 V/100 W halogen illumination source.

A 10 μl sample is sandwiched between thin 1.8 mm thickness glass plates and 0.17 mm thickness cover glass. The sandwiched-sample is then placed on microscope stage. The light passing through the darkfield condenser lens illuminates the sample with an intense cone shape. The cone-shaped light condenses at the sample from the side such that the apex is in the field of view. Thus, the only scattered light on ferromagnetic nano-particles using the darkfield condenser lens gathered and formed the image.

Microscope magnifications of 1000× images were detected by a digital video camera. The scattered speck images from ferromagnetic nano-particles were recorded in the memory. The digital images recorded in the memory were then input into a personal computer. Thereafter, the Brownian motion was analyzed by an image processing technique applying the PTV. The detail of the experimental apparatus is also discussed by Kikura et al. [5].

3. Results and discussion

Using the darkfield microscope system, a strong scattering-light was obtained in the water-based magnetic fluid. Twinkling and randomly moving specks were also observed. These specks represent primary clusters as pointed out by Nakatani [3], although darkfield observation does not allow the ferromagnetic nano-particle itself as 10 nm diameter.

Fig. 2 shows the vector field of primary clusters with 10 frames in the frame rate of 30 fps analyzed by the PTV in the water-based magnetic fluid with 12.7% weight concentration of ferromagnetic nano-particles. The PTV is a well-established technique utilized to measure fluid/particle velocity fields [6]. The technique is based on the measurement of small particles displacement agitated by
the Brownian motion. Velocity measurements were performed by recording two images of the particles in a motion-field separated by a specified time delay.

In Fig. 2, it is shown that each analyzed frame is resulted from two frames of particle motion. Although the numbers of particles were limited by the influence of the image contrast, the analysis results clarified that all the particles were satisfactorily observed in the image area. However, Fig. 2 also shows that the random walk of each primary clusters were observable in order to analyze the Brownian motion.

From the results of PTV analysis, velocity distribution of primary cluster was obtained. Fig. 3 show the velocity distributions of the particles analyzed by the PTV. Fig. 3 show that higher temperature results in higher velocity compared with the one at low temperature. The average velocity of 7.85 μm/s shown in Fig. 3(a) was lower than the average velocity of 8.19 μm/s shown in Fig. 3(b). Meanwhile, the average velocity of 8.76 μm/s shown in Fig. 3(c) was lower than the average velocity of 9.92 μm/s shown in Fig. 3(d). It is confirmed that the Brownian activity also depends upon the temperature.

Moreover, the average velocity shown in Fig. 3(c) was higher than that in Fig. 3(a). The same condition applies for the average velocity shown in Fig. 3(d) and (b). From this fact, it was confirmed that the Brownian motion in a magnetic fluid depends upon the concentration of ferromagnetic nano-particles. Fig. 4 shows the relation between temperature and mean particle velocity of primary cluster in a water-based magnetic fluid. The higher the concentration, the slower is the movement of the particles. Fig. 4 also contains the results for other conditions.

![Fig. 2. Vector field of ferromagnetic nano-particles in a magnetic fluid analyzed by PTV.](image)

![Fig. 3. Particle velocity distributions of primary cluster in a magnetic fluid.](image)
The Brownian motion is one of the important considerations when utilizing a sub-micron particle to trace fluid field for velocity field measurement. The random mean square particle displacement $s^2$ associated with Brownian motion for frame interval $\Delta t$ of the digital video camera is expressed as

$$\langle s^2 \rangle = 2D\Delta t$$  \hspace{1cm} (1)

where the Brownian diffusion coefficient $D$, first derived by Einstein (e.g. see Ref. [7]), is given as

$$D = \frac{kT}{3\pi\mu d_p}$$  \hspace{1cm} (2)

Here, $d_p$ is diameter of particles, $k$ Boltzmann constant, $T$ absolute temperature of the fluid, and $\mu$ the dynamic viscosity of the fluid. Using Eqs. (1) and (2), it is possible to evaluate the particle size from measured velocity of the particle $V(=\sqrt{\langle s^2 \rangle/\Delta t^2})$, which is calculated by PTV applying the following equation,

$$d_p = \frac{2kT}{3\pi\mu V^2\Delta t}.$$  \hspace{1cm} (3)

To verify the current particle size evaluation using Eq. (3), experiments were performed using the standard polystyrene particles (Polystyrene Uniform Microspheres, Duke Scientific, Cat. No 3200A, 3350A and 3500A) having a density of 1.05 g/cm$^3$. The size of these particles specified by the manufacturer on the basis of electron microscopic analysis is shown in Table 1. The Brownian motion is intensified with the decrease in particle size.

Table 1
Specification of standard particles

| Catalog no. | 3200A     | 3350A     | 3500A     |
|-------------|-----------|-----------|-----------|
| Nominal (nm)| 200       | 350       | 500       |
| Mean diameter (nm) | 199±6     | 343±9     | 499±5     |
| Standard deviation (nm) | 3.4       | 3.5       | 6.5       |
| Hydrodynamic diameter (nm) | 195–205   | 341–361   | 495–530   |

Fig. 5 presents the size distribution of 50 individual 200 nm particles produced by the PTV analysis of Brownian motion. The distribution parameters are as follows: mean size $d_{p\text{ mean}}=191$ nm with a confidence level of 95% and standard deviation of dev=$111$ nm. The results clarified that although its standard deviation is much larger, the mean size reasonably agree with the catalogue size. From this result, the following figures are plotted based on the result of mean particle size. Fig. 6 shows the relation between the mean cluster size from Eq. (3) and the theoretical values of particle size in different frame-rate of high-speed video camera using the standard polystyrene particles. In Fig. 6, it shows that the frame-rate dependent is quite small to measure the mean value of the primary cluster size.

Because the magnetic fluid is an opaque fluid, the image contrast would be too dark for conducting the velocity field’s measurement. Hence, for the measurement with high weight concentrations of 30 and 40 wt.% in water-based magnetic fluid, the PTV analysis was performed using a 150 W Metal Halide Lamp (Photron HVC-SL). Since the halide lamp has less ultra red light, it does not emit heat. Furthermore, it is also effective in counter measuring the heat, even under a very high light brightness of 340,000 lux at 1.0 m.
Because the primary cluster of the water-based magnetic fluid was assumed to be spherical, the measured mean particle size of primary cluster is shown in Fig. 7 as a function of weight concentration of ferromagnetic nano-particle in a water-based magnetic fluid. From Fig. 7, the mean size of primary cluster of the water-based magnetic fluid was almost in the same order with the result of Nakatani [3]. However, the size of primary cluster in the magnetic fluid was dependent upon the concentration of the ferromagnetic nano-particle. The reason for this concentration dependence is that during the dilution process to create a low concentration magnetic fluid, the agglomeration greatly occurred forming large primary clusters.

4. Concluding remarks

Thermal behaviour and particle size evaluation of primary clusters of ferromagnetic nano-particles in a magnetic fluid were investigated using an optical darkfield microscope system. Real-time observations of the Brownian motion of primary cluster in water-based magnetic fluids were examined. By using the Einstein’s equation for the Brownian motion and assuming that the primary cluster was spherical, the particle size evaluation obtained the size of primary cluster as 200 nm, which is good in agreement with the size obtained by Nakatani [3]. It is clarified that the primary cluster size in a water-based magnetic fluid is dependent upon the concentration of the ferromagnetic nano-particle.

References

[1] S. Chikazumi, S. Taketomi, M. Ukita, M. Mizukami, H. Miyajima, M. Setogawa, Y. Kurihara, Physics of magnetic fluids, J. Magn. Magn. Mater. 651 (1987) 245–251.
[2] S. Kamiyama, A. Satoh, Pipe-flow problem and aggregation phenomena of magnetic fluids, J. Magn. Magn. Mater. 85 (1990) 121–124.
[3] I. Nakatani, Direct observations on Brownian motions and agglomeration of magnetic particles in magnetic fluids, Proceedings of International Symposium on Hydrodynamics of Magnetic Fluids and its Applications, 1997, pp. 9–12.
[4] B. Jayadevan, I. Nakatani, Characterization of field-induced needle-like structures in ionic and water-based magnetic fluids, J. Magn. Magn. Mater. 201 (1999) 62–65.
[5] H. Kikura, J. Matsushita, M. Aritomi, Y. Kobayashi, K. Nishino, Micro visualization and PTV measurement of ferromagnetic particles, Proceedings of the Seventh International Symposium on Fluid Control, Measurement and Visualisation (FLUCOME’03), Sorrento, Italy CD-ROM Paper No. ID-152, 2003, pp. 1–6.
[6] K. Nishino, N. Kasagi, Turbulence statistics measurement in a two-dimensional channel flow using a three-dimensional particle tracking velocimeter, Proceedings of the Seventh Symposium on Turbulent Shear Flow, 1989, pp. 22.1–22.6.
[7] J.G. Santiago, S.T. Wereley, C.D. Meinhart, D.J. Beebe, R.J. Adrian, A particle image velocimetry system for microfluidics, Exp. Fluids 25 (1998) 316–319.