Journal of Magnetism and Magnetic Materials 322 (2010) 2525–2528

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

X-ray microtomography of field-induced macro-structures in a ferrofluid

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ARTICLE INFO

Article history:
Received 7 October 2009
Available online 23 March 2010

Keywords:
Ferrofluid
Agglomeration
Magnetic fluid
Field-induced cluster
Tomography

ABSTRACT

X-ray microtomography is used to visualize, in-situ, the three-dimensional nature of the magnetic field induced macro-structures (>1 μm) inside a bulk (~ 1 mm diameter) magnetite-particle–mineral oil ferrofluid sample. Columnar structures of ~ 10 μm diameter were seen under a 0.35 kG applied magnetic field, while labyrinth type structures ~ 4 μm in width were seen at 0.55 kG. The structures have height/width aspect ratios >100. The results show that the magnetite volume fraction is not constant within the structures and on average is considerably less than a random sphere packing model.

1. Introduction

Ferrofluids are a class of colloids where nano-sized (~ 10 nm diameter) magnetic particles are dispersed in a carrier fluid. They are a model system in the general class of dipolar fluids [1,2]. Ferrofluids have been used for vacuum seals, but lately, has been proposed for a multitude of new applications including heat transfer [3], micro- and nano-self-assembly [4–6] and biomedicine [7,8]. In a magnetic field, the particles tend to form chains [9] with the chain axis aligned with the field. The individual chains can coalesce and form thick and long 'macro'-sized structures whose sizes range from the tens of nm (few particles thick) to tens of micron (thousands of particle thick) in width and can span the sample cell in length. These macro-structures have been described as columns, labyrinths, or lamellar sheets, and can undergo structural phase transitions as a function of applied field [10]. Understanding these aggregation structures is important because the majority of ferrofluid applications depend on its flow properties. Although magnetoviscosity [11] has been explained [12,13] based on well-dispersed dilute ferrofluids (no particle–particle interactions), it has been suspected that the observed discrepancies for more concentrated and commercially available ferrofluids are due to the formation of chains and macro-structures [14].

Measurements of ferrofluid agglomeration are hampered by the fluid opacity to visible light. Optical microscopy measurements have been limited to thin films of ~ 10 s of microns [5,15–17], and/or to very dilute concentrations of magnetic particles [18]. Thin film measurements are subject to wall-effects [19,20] since the dimensions of the clusters can be in the 10–100 s μm range. Neutron [19,21,22] or X-ray [23] scattering have provided nm-scale information regarding the magnetic particles and their near neighbors. However, the interpretation of these bulk measurements is very challenging in multiphase systems such as the one in this study [22]. These challenges have led to efforts where the ferrofluid is fixed by use of resins [24], cryogenic freezing [25,26] or by evaporation of the carrier [4,27,28]. These 'fixing' techniques have the significant disadvantage that the measurements most likely do not reflect the structure in its natural fluid state. There has not been any experimental measurement of the *local* spatial density or concentration variations of the magnetic particles across (inside or outside the macro-structures) the fluid sample. These quantities are crucial if one is to either model the fluid system or to validate the results from theoretical or computational models. In this paper, we present the first direct quantitative three-dimensional measurement of field-aligned macro-structures in a bulk ferrofluid.

2. Material and methods

The measurements were performed at the Advanced Photon Source XOR 32-ID beamline using 25 keV X-rays. A commercial ferrofluid (EFH1, Ferrotec, USA) was used, together with a commercial mineral oil (Cat. S55667, Fisher Scientific, USA) for dilution. The manufacturer only states that EFH1 contains magnetite (Fe_3O_4) particles in a mineral oil carrier. Samples were contained in small glass tubes (OD = 1.75 mm, ID = 1.24 mm) and aligned vertically to the tomography rotation axis. A small disc permanent magnet (NdFeB, 12.5 mm diameter, 3.2 mm thick) was placed at the bottom of the glass tube and plastic spacers were placed between the magnet and the sample to vary the field strength at the sample position. Magnetic fields were measured with a gaussmeter (Model 410 Gaussmeter, Lakeshore Inc., USA). At a constant height above the magnet, the magnetic field variation was $<3\%$ over the cross-sectional area of the glass

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doi:10.1016/j.jmmm.2010.03.012

tube. Along the sample tube axis, the magnetic field varies by ~20% per mm. This large vertical field gradient results in a magnetite concentration gradient in the sample (see Section 3). The X-rays are detected by a cerium-doped yttrium aluminum garnet scintillator and imaged on a charge-coupled-device (CCD) camera (Sensicam, Cooke Corporation, USA) via a 5× microscope objective (Mitutoyo, Japan) and tube lens. The camera has 1024 × 1280 (vertical × horizontal) pixels with 6.7 × 6.7 μm^2 pixel size. The demagnified pixel size was 1.46 × 1.46 μm^2. Projection images were acquired every 0.125°. Tomographic reconstruction was performed using GRIDREC [29].

3. Results and discussion

X-ray projections, reconstructed cross-sections and 3D renderings of the samples under two different applied magnetic field strengths are shown in Fig. 1. The columnar or labyrinth structures are not uniformly distributed across the glass tube. The macro-structures are preferential to the side walls of the container. This is likely due to wall effects [19,20] from the negative susceptibility of the borosilicate glass tube. The heights of the structures are shorter for the higher field case (Fig. 1a and d); approximately 670 μm vs 1050 μm. Height/width aspect ratios are >100; larger than those observed thus far with thin films. At half-height, the widths of the structures are ~10 μm for the columns (Fig. 1a–c) and ~4 μm for the labyrinths (Fig. 1d–f). There is no measurable difference between the attenuation coefficients of the column and labyrinth structures. In both cases, the macro-structures begin to split apart near the bottom (Fig. 2). Similar splitting has been observed in a magnetorheological fluid where the particle sizes are 30 × (0.3 μm) bigger [30].

X-ray attenuation coefficients from tomography reconstructions are susceptible to artifacts [31,32]. To evaluate the accuracy of the attenuation coefficients obtained in this study, we compare the measured attenuation values of the borosilicate glass tube and for a sample of pure EFH1 where no macro-structures were

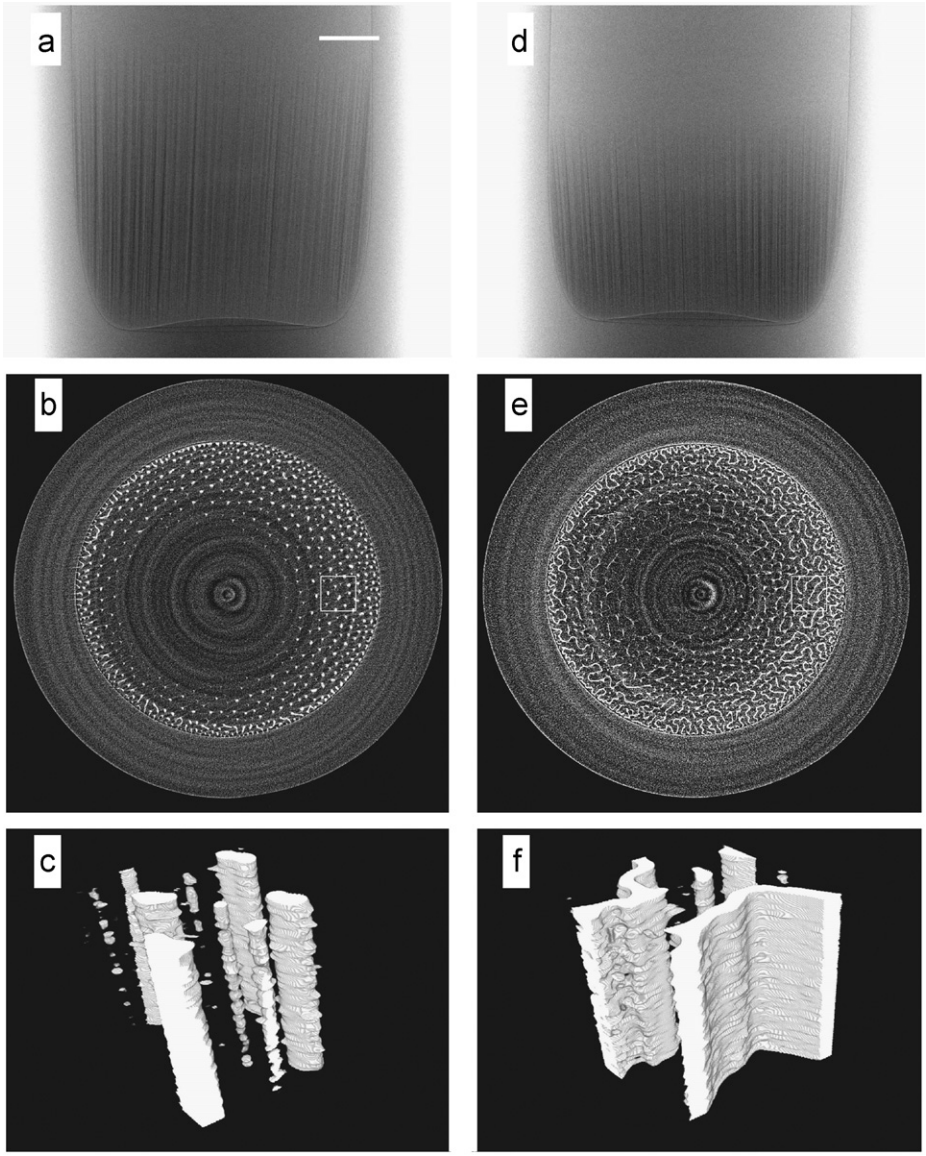

Fig. 1. Flat-fielded projection images (a and d), reconstruction slices (b and e) and 3D renderings (c and f) for a 1:4 diluted sample of EFH1 under 0.35 kG (a–c) and 0.55 kG (d–f) applied field. In b and e, the ring structures are artifacts from the reconstruction. In a and d, white indicates higher transmission; in b and e, white indicates a higher attenuation coefficient. c and f are rendered from 60 slices (1.46 μm per slice) of binarized reconstructions. Scale bar in (a) is 250 μm and applies to a, b, d and e. Small boxes in b and e indicate the location for the contour plots shown in Fig. 2.