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Initial susceptibility and viscosity properties of low concentration ε-Fe₃ N based magnetic fluid

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Abstract In this paper, the initial susceptibility of ε-Fe₃N magnetic fluid at volume concentrations in the range $\Phi = 0.0 \sim 0.0446$ are measured. Compared with the experimental initial susceptibility, the Langevin, Weiss and Onsager susceptibility were calculated using the data obtained from the low concentration ε-Fe₃N magnetic fluid samples. The viscosity of the ε-Fe₃N magnetic fluid at the same concentrations is measured. The result shows that, the initial susceptibility of the low concentration ε-Fe₃N magnetic fluid is proportional to the concentration. A linear relationship between relative viscosity and the volume fraction is observed when the concentration $\Phi < 0.02$.

Keywords Magnetic fluid · Nano-material · Initial susceptibility · Viscosity

Introduction

Magnetic fluid (MF) is stable colloidal suspensions composed of single-domain magnetic nanoparticles dispersed in appropriate solvents. In order to prevent agglomeration due to attractive Van der Waals or magnetic dipole–dipole interactions, the nanoparticle surface is covered with chemically adsorbed surfactant molecules (steric stabilization) or is electrically charged (electrostatic stabilization) [1]. Owing to

their unique physical and chemical properties, these ferromagnetic liquids have attracted wide interest since their inception in the late 1960s.

In a sufficiently diluted ferrofluid, the magnetic particles can be thought of as noninteracting, and the magnetic properties of such a ferrofluid are similar to those of an ideal paramagnetic gas. The difference is that the large dipole moment of individual nanoparticles, which are generally more than three orders of magnitude larger than that of atomic dipole moments in paramagnets. In practical magnetic fluid, the interactions between nanoparticles can not be ignored and great interests have been paid on the dipolar interacting particles [2, 3].

Interactions in ferrofluid can be experimentally investigated with magnetic susceptibility and viscosity measurements. Various theoretical and experimental studies on initial susceptibility [4–8] were introduced about magnetic fluid. Several ideal models have been developed to describe the initial susceptibility of the magnetic colloid, such as Langevin model [5– 7], Weiss model [8] and Onsager theory [9]. The Langevin model assumes that the magnetic fluid consists of Brownian, monodisperse, noninteracting spheres, each having a permanent magnetic moment, which rotates together with the particle to align to an external magnetic field. For the initial susceptibility, the earliest model of a self-interacting magnetic medium is the mean-field Weiss model [8]. A similar early approach to the problem of a self-interacting magnetic medium is the Onsager theory [9] originally conceived for polarizable molecules. The presence of magnetic particle in a fluid increases internal friction when it is flowing. From the point of view of continuum mechanic, the viscosity of magnetic fluid is greater than that of carrier liquid.

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The viscosity properties of magnetic colloids were introduced in ref. [7, 10].

In this paper, various low concentrations of ε-Fe₃N magnetic fluid samples were synthesized with the method introduced in ref. [11]. After that, we measure the initial susceptibility, saturation magnetization and viscosity of the low concentrations ε-Fe₃N magnetic fluid samples. Compared with the experimental initial susceptibility, the Langevin, Weiss and Onsager susceptibility were calculated using the data obtained from the low concentration ε-Fe₃N magnetic fluid samples. The viscosity properties of the samples are also studied.

Experimental

Materials

ε-Fe₃N based magnetic fluid was synthesized according to the method reported in ref [11]. The carrier liquid was composed of α-olefinic hydrocarbon synthetic oil (PAO oil with low volatility and low viscosity) and succinicimide (surfactant). The stock ε-Fe₃N magnetic fluid had a high concentration, from which we obtained other low concentration samples by dilution with the carrier liquid. These diluted samples were ultrasonic agitated about 1 h to ensure the homodisperse of magnetic particles. The image of carrier liquid (0) and six ε-Fe₃N magnetic fluid samples (1–6) is present in Fig. 1.

Volume fraction of solids

The concentration of the MF samples is determined as following method. First we measure the mass M of a certain volume V_F of the sample. If there is a volume V_P of pure material of ε-Fe₃N in the sample then the volume of carrier fluid with surfactant would be V_F–V_P. Measuring the density of the carrier fluid ($\rho_C = 0.846$ g/cm³), magnetic fluid (ρ_F) and knowing the density of pure ε-Fe₃N ($\rho_P = 6.88$ g/cm³), then

$$(V_F - V_P)\rho_C + V_P\rho_P = M \tag{1}$$

dividing the Eq. (1) by V_F, and knowing that physical volume fraction $\Phi = V_P/V_F$, we get

$$\Phi = \frac{\rho_F - \rho_C}{\rho_P - \rho_C} \tag{2}$$

where ρ_F is the density of magnetic fluid sample. The density of the fluid was measured using a picnometer at $20 \pm 1°$ C.

Transmission electron microscopy (TEM)

The size and morphology of ε-Fe₃N nanoparticles were obtained using a 2100fx transmission electron microscope (TEM) operated at 200 keV. TEM sample was prepared by dispersing the particles in alcohol using ultrasonic excitation, and then transferring the nanoparticles on the carbon films supported by copper grids. In Fig. 2a, the magnetic particles form intricate annular long chains under the influence of the electromagnetic field in TEM. There are some large particles whose shapes differ from spherical in magnetic fluid (see Fig. 2b). Image analysis on particles in Fig. 2b yielded an average size of $d_{TEM} = 14 \pm 2$ nm.

Magnetic measurement

The magnetization curves of magnetic fluid samples were measured with a LDJ9500 Vibrating Sample Magnetometer (VSM). The initial susceptibility of the
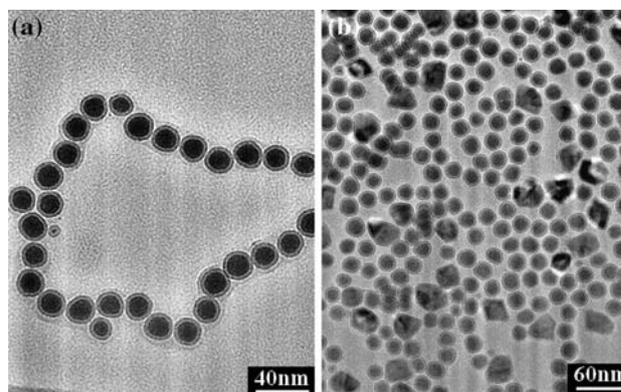

Fig. 1 Images of the carrier liquid (0) and different concentration magnetic fluid samples (1–6)

Fig. 2 TEM images of ε-Fe₃N magnetic particles

magnetic fluid samples was measured with VSM in the magnetic field intensity range, 0 ~ 20Oe. The sample holder is in the shape of a cylinder and a ratio between the height and diameter equal to 3. Due to the low concentration of the particle in the samples, and the high aspect ratio of the cylinder, the demagnetizing field is negligible. All the diluted samples are measured immediately after preparation at 300 K.

Calculation on initial susceptibility

Figure 3 gives the magnetization curves of the magnetic fluid samples (1, 2). Both of the samples exhibit superparamagnetic behavior as indicated by zero coercivity and remanence, from which we also able to extract particle size information. Chantrell et al. [12] showed that the magnetic particle size (d_m) and size distribution (σ) could be estimated from the magnetization curves using the formula

$$d_m = \left(\frac{18 k_B T}{\pi M_d} \left[\frac{\chi_i}{3 \Phi M_d H_0} \right]^{1/2} \right)^{1/3} \tag{3}$$

$$\sigma = \frac{1}{3} \left(\ln \left(\frac{3 \chi_i H_0}{\Phi M_d} \right) \right)^{1/2} \tag{4}$$

respectively, where M_d (123emu/g [13]) is the saturation magnetization of bulk material and Φ is the particle volume fraction. The initial magnetic susceptibility (χ_i) is obtained from the low field curve by using $\chi_i = (dM/dH)_{H \to 0}$ while H_0 is obtained from the same curve at high external fields where M versus $1/H$ is linear with an intercept on the M axis of $1/H_0$. The magnetic diameter of particles in every magnetic fluid samples is calculated and is about $d_m = 12 \pm 2$ nm which deviates significantly from the physical diameter ($d_{TEM} = 14 \pm 2$ nm)
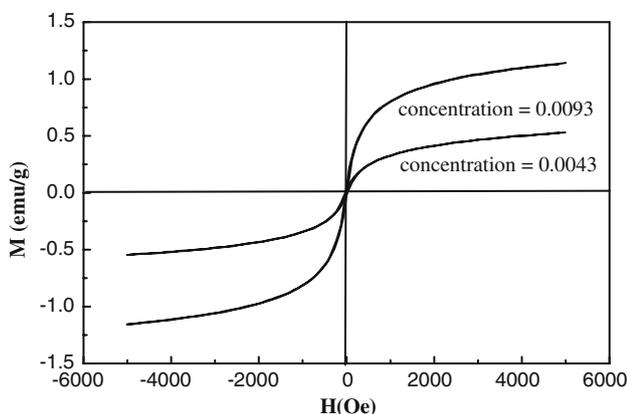
obtained with TEM (see Fig. 2). Similar results have been reported for a number of magnetic fluids [12, 14] and have been attributed to the existence of non-magnetic layer on the particle surface.

Accord to ref. [4], ideal Langevin initial susceptibility can be calculated using Eq. (5)

$$\chi_{iL} = \frac{\mu_0 \pi M_d^2 d_m^3 \Phi_m}{18 k_B T} \tag{5}$$

where μ_0 is the magnetic permeability of vacuum, d_m is the magnetic diameter which can be obtained from Eq. (3). And the magnetic volume fraction value Φ_m is different from the physical volume fraction due to the existence of nonmagnetic layer at the surface of the particles. The magnetic fraction of solid particles and the nonmagnetic layer of the particles can computed from ref. [15]

$$\Phi_m = \Phi \frac{d_m^3}{(d_m + \delta)^3} \tag{6}$$

where δ is the nonmagnetic layer and is estimated to be 2.0 nm from TEM. Substituting Φ_m, magnetic diameter (d_m) and M_d into Eq. (3) we get the Langevin initial susceptibility. The Langevin initial susceptibility of the samples was obtained and shown in Fig. 4.

According to Weiss model for magnetic fluid [8], Weiss initial susceptibility of a self-interacting magnetic medium was deduced in [16]:

$$\chi_{iW} = \frac{\chi_{iL}}{1 - \chi_{iL}/3} \tag{7}$$

where χ_{iL} is Langevin initial susceptibility.

In Onsager's theory [9], divergence of the dielectric constant is absent, in accordance with experience. The susceptibility following from this model is
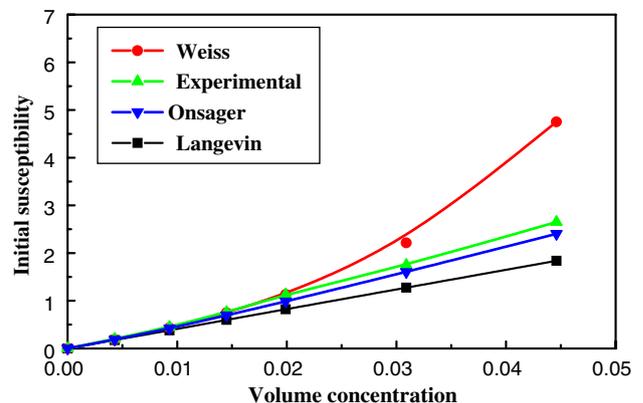

Fig. 3 Magnetization curves of the ε-Fe$_3$N magnetic fluid (sample 1 and 2) measured at 300 K

Fig. 4 The relationship between concentration and initial susceptibility

$$\chi_{iO} = \frac{3}{4}\left(\chi_{iL} - 1 + \sqrt{1 + \frac{2}{3}\chi_{iL} + \chi_{iL}{}^2}\right) \qquad (8)$$

Viscosity measurement

The viscosity measurements of the samples (0 ~ 6) were carried out using a NDJ-7 rotation viscosimeter directly. The temperature of the sample cup was maintained at 20 ± 1 °C. The instrument was calibrated using a Brookfield viscosity standard fluid. The density, viscosity, particle volume fraction, and magnetic volume fraction of the magnetic fluid samples are shown in Table 1.

Result and discuss

Initial susceptibility

In Fig. 4, the theoretical susceptibility of various concentration magnetic fluid samples were calculated using different models mentioned above. From Fig. 4, we can see that none of the models mentioned above appears to describe the experimental data very well. In a sufficiently diluted ferrofluid (sample 1 and 2), magnetic dipolar interactions are neglected and the magnetic particles of the ferrofluid feel only the external magnetic field. And the susceptibility increases linearly with volume fraction according to Eq. (5). As expected, dipolar interactions may cause particle aggregate which lead to non-Langevin behavior at high concentrations (sample 3, 4, 5 and 6). The ferrofluid particles are not identical, and they differ both in size and magnetic moment. The system of polydisperse (see Fig. 2), where the particles have different hard sphere diameters and/or carry different magnetic moments can also lead to the deflection between the experimental value and Langevin susceptibility since initial susceptibility (χ_i) is more sensitive to the larger particles [12].

Compared with the three models, the Onsager's theory is the closest to the experimental data. In this model, magnetic fluid can be regarded as a self-interacting magnetic medium with susceptibility. In Onsager' theory [9], spherical molecules occupy a cavity in a polarizable continuum. The field acting on molecule is the sum of a cavity field plus a reaction field that is parallel to the actual total (permanent and induced) moment of the molecule. Self-interacting is permitted in Onsager' theory, that is similar to real magnetic fluid.

As is shown in Fig. 4, the Weiss model works well for low concentrated ferrofluid but strongly overestimates the initial susceptibility of concentrated ferrofluid. The Weiss theory is based on the idea that each dipole experiences an effective magnetic field H_{eff}, which is composed of the externally applied field H_{ext} plus a additive field kM due to all other dipoles. In liquids, the value of k is determined by the shape of the imaginary cavity in which each dipole is thought to reside. For a spherical cavity k is 1/3 and Eq. (7) was obtained [16]. According to the theory, when the particle volume fraction is low, each dipole experiences effective magnetic field H_{eff} mainly from externally applied field H_{ext} and the additive field kM caused by all other dipoles is very small. The value of Weiss susceptibility is close to Langevin initial susceptibility. When the concentration increases, the additive field kM enhances quickly and the initial susceptibility is strongly over estimated.

Viscosity properties

The density, viscosity, concentration of the fluids was presented in Table 1. The value of $(\eta-\eta_0)/\eta_0$ and $\frac{(\eta-\eta_0)/\eta_0}{\Phi}$ were also calculated in Table 1 where η is the viscosity of magnetic fluid samples (1–6) and η_0 is the viscosity of carrier liquid (0). From Table 1, we can see that the density and viscosity of the sample increased gradually with increasing particle concentration. For the first four magnetic fluid samples, the difference between the values of $\frac{(\eta-\eta_0)/\eta_0}{\Phi}$ is little and the mean

Table 1 The density (ρ_F), viscosity (η), particle volume fraction (Φ), and magnetic volume fraction (Φ_m) of the magnetic fluid samples. $\eta_0 = 50$ mPa s is the viscosity of carrier liquid (0). All the density (ρ_F) and viscosity (η) was measured at 20 ± 1 °C

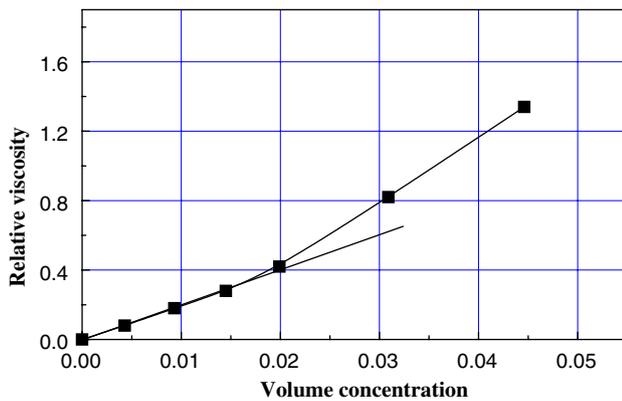| Samples	Density (g/cm^3)	Viscosity (mPaS)	Volume fractionΦ	Magnetic volume fraction Φ_m	Relative viscosity$(\eta-\eta_0)/\eta_0$	$\frac{(\eta-\eta_0)/\eta_0}{\Phi}$
0	0.8460	50	0	0	0	0
1	0.8721	54	0.0043	0.0027	0.08	18.60
2	0.9024	59	0.0093	0.0059	0.18	19.35
3	0.9336	64	0.0145	0.0091	0.28	19.31
4	0.9664	71	0.0199	0.0125	0.42	21.10
5	1.0330	91	0.0309	0.0195	0.82	26.53
6	1.1150	117	0.0446	0.0281	1.34	30.04

Fig. 5 Relation between relative viscosity and concentration of ε-Fe$_3$N magnetic fluid.

value of $(\eta-\eta_0)/\eta_0$ is 19.59. Figure 5 shows the relation between relative viscosity $(\eta-\eta_0)/\eta_0$ and concentration (Φ). From Fig. 5, we can clearly see that the slope of the curve approach to 19.59 when $\Phi < 0.02$ (first four magnetic fluid samples), which means that

$$\frac{(\eta - \eta_0)/\eta_0}{\Phi} \approx 19.59 \qquad (9)$$

So, we can approximately obtain the following equation

$$\eta = \eta_0(1 + 19.59\Phi) \qquad (10)$$

As we known that, for isotropic diluted suspensions with non-magnetic uncoated spherically shaped particles, Einstein (1906, 1911) showed that the dependence of viscosity of a suspension on the volume fraction may be represented by [10]:

$$\eta = \eta_0(1 + 2.5\Phi) \qquad (11)$$

This relationship is valid only for small concentrations. As mentioned above, Eq. (11) is only correct when there is no interaction between the uncoated spherically shaped dispersed particles. In order to discuss conveniently, Eq. (12) which is in the same form as Eq. (10) and Eq. (11) is assumed:

$$\eta = \eta_0(1 + a\Phi) \qquad (12)$$

In this magnetic fluid system, there are several reasons that lead to the increase of the coefficient a. First, in Einstein's relationship Eq. (11), the solid particles are nonmagnetic and there is no interaction between dispersed particles. In magnetic fluid, in addition to the hydrodynamic interaction, there exists the dipolar–dipolar interaction affecting their relative motion and

the viscosity of magnetic fluid must be determined by the level of this interaction; Second, real magnetic fluid may differ considerably from the simplest model presenting particles as nonintercating monodisperse spheres. From the TEM image (see Fig. 2), the samples include some amount of large particles, and the shape of which differs essentially from spherical. The shape anisotropy of non-spherical particles will hinder the free rotation of the particles and therefore the viscosity of the fluid increases. Moreover, due to the magnetic interaction, the formation of agglomerates, chains and other structures will decrease the internal rotation of the magnetic particles and it will give rise to viscous behavior of magnetic fluid. Third, in order to prevent agglomeration, every particle in the fluid is covered with a surfactant layer (see Fig. 2) that is different from the assumption of Eq. (11). The surfactant layer will also enhance the rotation resistance of the magnetic particles in the fluid. All the reasons mentioned above will increase the coefficient a. When $\Phi > 0.02$, the coefficient a increases quickly (see Fig. 5) and this may be caused by the high concentration of particles.

Conclusion

The initial susceptibility of ε - Fe$_3$N magnetic fluid at concentrations in the range $\Phi = 0.0 \sim 0.0446$ are measured. The Langevin, Weiss and Onsager susceptibility were calculated using the data obtained from the low concentration ε-Fe$_3$N magnetic fluid samples. When $\Phi < 0.0145$ (sample 1 and 2), the experimental initial susceptibility (χ_i) agrees well with the three models. For the dipolar interactions, χ_i lead to non-Langevin behavior at high concentrations when $\Phi > 0.0145$ (sample 3, 4, 5 and 6). Weiss model strongly overestimates the initial susceptibility of concentrated ferrofluid that may because of magnifying the additive field kM caused by all other dipoles. Onsager's theory is the closest to the experimental data when considering the self-interaction between magnetic particles. Viscosity measurements of ε-Fe$_3$N ferrofluid have been made for six different concentrations including the carrier liquid. Similar to Einstein's viscosity formula Eq. (11), the linear relationship between the relative viscosity and the concentration is observed. The factors such as dipolar–dipolar interaction, shape anisotropy, magnetic agglomerate, chains-structure and surfactant layer lead to the strong increase of the coefficient a.

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