

# The Effect of Gelation on the Apparent Magnetism of ZnFe<sub>2</sub>O<sub>4</sub> Sol-Gel Systems

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## Abstract

Experiments have shown that for thixotropic sol–gel systems consisting of ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles without any matrix material, the measured magnetization, or susceptibility of gels, are greater than those of sols. For the reduced susceptibility, a system with a volume fraction of particles of  $\phi_v=2.0\%$  is lower than a system with  $\phi_v=1.5\%$ . These results have been interpreted in terms of a magnetization mechanism based on the Brownian rotation of the moments fixed inside the colloidal particles, which would be dramatically affected by the non-magnetic hydrodynamic interaction. For weakly cross-linked gels, the translational degree of freedom is “frozen” while the rotational degree of freedom remains unchanged, so that their hydrodynamic interaction effect is weaker, and they are more easily magnetized than the sols with both rotational and translational degrees of freedom. The action of gelation preventing the hydrodynamic interaction effect on the magnetization process can be referred to as the “gelation decoupling”. Correspondingly, such behavior of the hydrodynamic interaction in affecting the apparent magnetism can be referred to as a “viscomagnetic effect”.

**Keywords:** sol, gel, magnetism, hydrodynamics, interaction

## 1. Introduction

Magnetic sols, also known as ferrofluids, magnetic liquids, magnetic colloids, etc., are suspensions of magnetic nanoparticles with a mean diameter of about 10 nm in a non-magnetic carrier liquid. Such systems have been extensively studied since the 1960s due to their novel magnetically-controlled properties (Odenbach, 2009). A remarkable feature of magnetic sols is its ability to change their hydrodynamic (rheological) properties under the action of an external magnetic field, which is referred to as a magnetoviscous effect (Zubarev & Chirikov, 2010). For spin-up of colloidal ferrofluids in a rotating magnetic field, the fluid motion depends on non-equilibrium magnetization (Rosensweig, Popplewell, & Johnston, 1990). In many investigations, the apparent magnetism of magnetic sols has generally been regarded as depending on the magnetic interaction between like particles as dipoles. However, Zhang and co-workers noted an effect of hydrodynamic interaction on alternating current susceptibility (Zhang, Boyd, & Luo, 1996).

Gels sensitive to electric or magnetic fields are of interest as “smart” materials with unique potential applications (Tanaka et al., 1982; Qsada et al., 1992; Barsi et al., 1996; Suto et al., 2009; Leveis et al., 2010). Typically, magneto-sensitive gels consist of magnetic nanoparticles dispersed in an organic or inorganic matrix (Chaput et al., 1993; Li et al., 1999; Bentivegna et al., 1999; Casas et al., 2002; Bohlius et al., 2004; Galicia et al., 2011). As for magnetic sols, the novel magnetic features of such gels stems from the magnetic properties of the nanoparticles. Each particle is a magnetic monodomain, that is to say, it has a paramagnet magnetic dipole, the intensity of which is fixed, depending on the nature of the constituent material, but the direction can fluctuate inside the particle. In such magnetic gels, the magnetic phase is captured in the non-magnetic network of the organic/inorganic gel. Such magnetic gels, prepared by suspending magnetic nanoparticles in a non-magnetic matrix, are clearly binary composite systems (Teixeira et al., 2003) rather than conventional gels, and their magnetic properties may be influenced by the matrix material (Bohlius et al., 2004). A few magnetic gels based on iron oxide nanoparticles without any matrix material have been investigated with regard to the dynamics of gelation and have been characterized (Ponton et al., 2002; Liu et al., 2006). Compared with solidified magnetic sols (frozen ferrofluids) (Kötitz et al., 1995; Hrianca., 2002), in a gel the translational motion of the colloid particles, which is a main feature of magnetic sols, is inhibited to the same extent, but the rotation of the particles

themselves is not restricted since magnetic gels are usually only weakly cross-linked (Jarkova, Pleiner, Müller, & Brand, 2003). Therefore, magnetic gels may exhibit different magnetic behavior compared to fluids (sols) and solids (frozen fluids). The macroscopic behavior of a material depends on its microstructure, and hence studies of the magnetic behavior of magnetic sol-gel systems may not only be valuable for natural physical research of complex fluids, but may also lead to potential applications. Nevertheless, reports on investigations of magnetic gels have been far fewer than those on magnetic sols.

A thixotropic fluid has the property of being in a gel state at equilibrium. If it is mechanically sheared or shaken above a given threshold, it becomes a flowing liquid, but the gel will regenerate if the sample is left to stand (Ponton et al., 2002). Experiment shown that  $\text{ZnFe}_2\text{O}_4$  nanoparticles based colloids can self-form thixotropic sol-gel system (Li et al., 2009). Due to lack any matrix or additive, such system's magnetism results only from the colloidal particles, so the system is suitable in particular to be used to investigate the relation between macroscopic behaviors and microstructure. In the work presented herein, thixotropic sol-gel systems based on  $\text{ZnFe}_2\text{O}_4$  nanoparticles have been prepared, and the effect of hydrodynamic interactions on the apparent magnetism has been revealed by comparing the magnetization behaviors of both the sols and gels.

## 2. Experimental

Bulk  $\text{ZnFe}_2\text{O}_4$  is an antiferromagnetic material and its nanoparticles can exhibit superparamagnetic or weak ferromagnetic properties since net spins can exist on their surfaces (Schnele & Deetscreek, 1962) or be induced by point defects (Wu, Mao, Ye, Xie, & Zheng, 2010). Spherical  $\text{ZnFe}_2\text{O}_4$  nanoparticles were produced from an aqueous mixture of  $\text{ZnCl}_2$  and  $\text{FeCl}_3$  by a co-precipitation method. The crystal structure and morphology of the as-prepared particles were characterized by X-ray diffraction analysis (XRD, XR-2) and transmission electron microscopy (TEM, Philips Technai 10), as shown in Figure 1. Statistical analysis indicated that the size of the particles fit a log-normal distribution with a median diameter  $d_g$  of 4.22 nm and a standard deviation  $\ln\sigma_g$  of 0.26. The diameter of average volume,  $d_v$ , obtained from the expression  $d_v = \exp(\ln d_g + 1.5 \ln^2 \sigma_g)$  (Granqvist & Buhrman, 1976), was 4.67 nm.

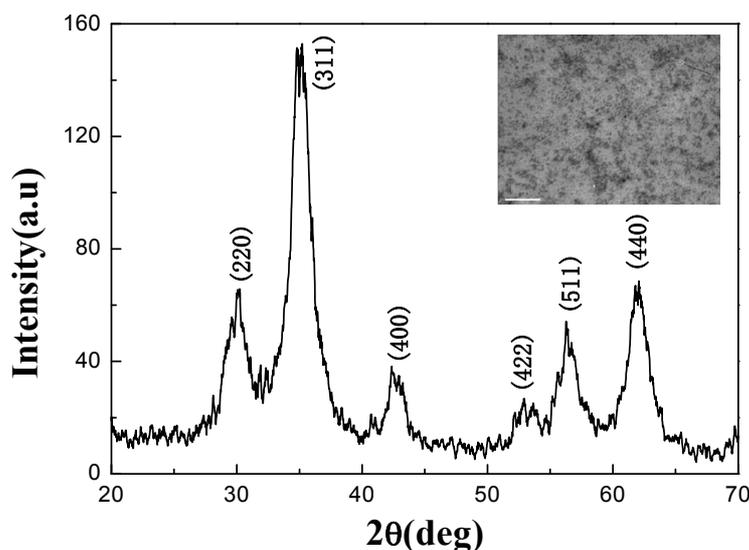


Figure 1. X-ray diffraction spectrum of the particles. The inset shows a typical micrograph of the particles (size bar 50 nm)

The sol-gel systems were synthesized by a similar method to that used to prepare self-formed  $\text{CoFe}_2\text{O}_4$  ionic ferrofluids (Li et al., 2007), whereby the ferrofluid is formed through self-ionization of the nanoparticles and letting the metal ions absorb on the remaining part of the particles to prevent aggregation by electrostatic repulsive force. In this method, dilute aqueous  $\text{HNO}_3$  solution is used as the carrier liquid to form acid ferrofluids. The concentration of  $\text{HNO}_3$  ( $S$ ) is dependent on the volume fraction of the particles  $\phi_v$  for synthesizing  $\text{ZnFe}_2\text{O}_4$  sol-gel systems, i.e.:

$$S = \frac{3\rho_p}{Z_s M_{ws}} \cdot \frac{\phi_v}{1 - \phi_v} Q \quad (1)$$

where  $\rho_p$  is the density of  $\text{ZnFe}_2\text{O}_4$ ,  $Z_s$  is the valence of nitric acid,  $M_{ws}$  is the molecular weight of  $\text{ZnFe}_2\text{O}_4$ , and  $Q$  is an experimentally determined parameter. For the formation of thixotropic  $\text{ZnFe}_2\text{O}_4$  gels, the  $Q$  value is 0.3 when  $\phi_v$  is 1.5–2.0%, and the pH is about 1.5, as measured by means of a pH meter (HDP-9522 BT type). After 24 h, the  $\text{ZnFe}_2\text{O}_4$  sol fluids (as shown in Figure 2 (a)) were transformed into non-fluid gels (as shown in Figure 2(b)). The formation of  $\text{ZnFe}_2\text{O}_4$  sol–gels differs from that of  $\text{SnO}_2$  sol–gels, for which polyvinyl alcohol (PVA) was added to induce gelation (Santos, Santilli, & Pulcineli, 1999), and no polymer's action need be considered for gelation of the  $\text{ZnFe}_2\text{O}_4$  system.

The magnetization curves of the sol–gel systems with  $\phi_v=1.5$  and 2.0% were measured by means of a vibrating sample magnetometer (VSM, HH-15) by sweeping the magnetic field at room temperature. For the measurement, the sol samples were freshly broken-up by mechanical shaking for 0.5 h using an IKA-KS130 basic apparatus set at MOT 720 rpm, and transferred to plastic tubes of diameter 1.5 mm and length 8.0 mm. After sealing the tubes, the sols were left to stand for 24 h to form the gel samples for the measurement of magnetization.

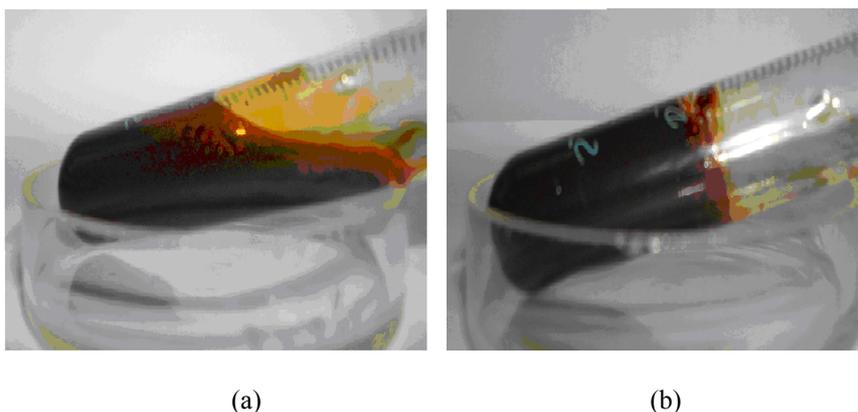


Figure 2. Photographs of (a) the  $\text{ZnFe}_2\text{O}_4$  sol with  $\phi_v=2.0\%$  and (b) the gel formed after 24 h

### 3. Results and Analysis

Figure 3 presents the magnetization results, from which it can be seen that the magnetization curves of the sol and gel samples do not coincide with each other, with the former lying below the latter. Since the same magnetic phase was present in the sol and gel samples, the difference in their apparent magnetization curves implies that the gel was more easily magnetized than the sol. In addition, it is noticed that for the sol–gel system, all magnetization curves corresponding to an increase and decrease of the field did not exhibit hysteresis loops, and the magnetization curves were the same when the field reversed. Thus it is judged that the sols and gels all achieved the thermodynamic equilibrium state during measurements of the magnetization curve during magnetic field sweeps. Therefore, it can be concluded that the respective samples underwent different magnetization processes.

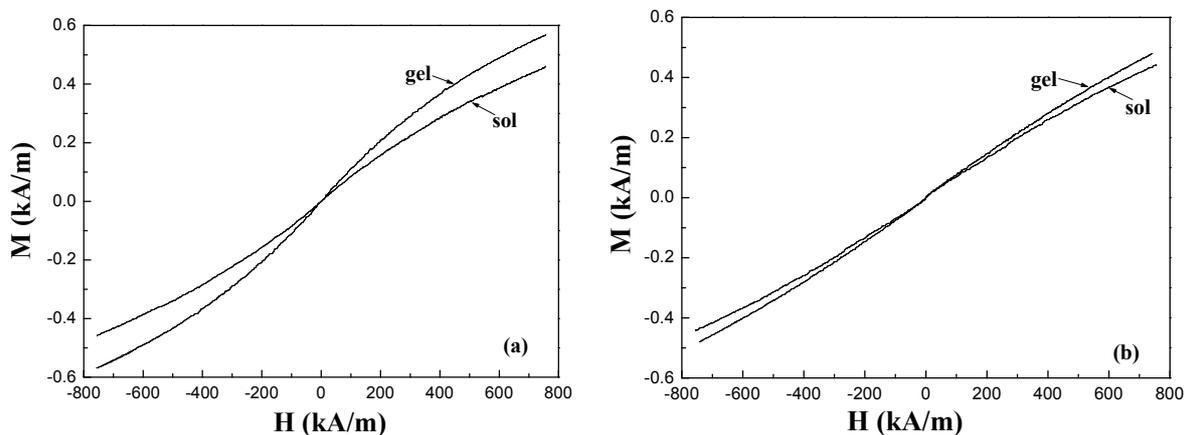


Figure 3. Magnetization curves of the sol-gel systems with (a)  $\phi_v = 1.5\%$  and (b)  $\phi_v = 2.0\%$

The difference in the apparent magnetization behavior can be clearly discerned from the susceptibility curves of  $\chi(=M/H)$  vs.  $H$ , as shown in Figure 4. It can be seen that in the low-field regime ( $|H| < 50$  kA/m), these curves exhibit obvious fluctuations (as shown in the insets in Figure 4), but that when  $|H|$  exceeds 50 kA/m, these susceptibility curves tend to decrease with the field strength. The susceptibilities of the sols were lower than those of the gels.

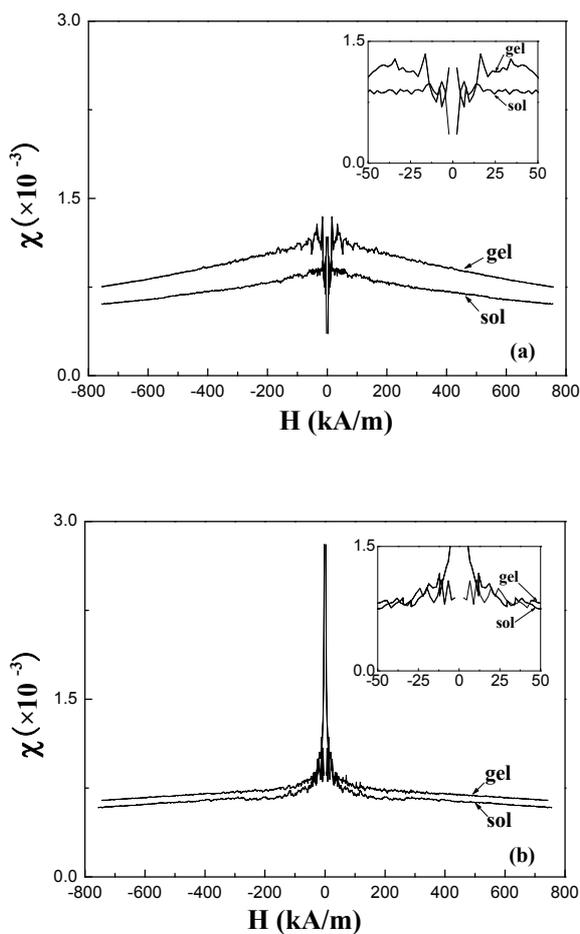


Figure 4. Susceptibility curves for the  $ZnFe_2O_4$  sol-gel systems with (a)  $\phi_v = 1.5\%$  and (b)  $\phi_v = 2.0\%$

#### 4. Discussion

The behavior of the apparent susceptibilities indicates different interparticle interactions affecting the magnetization processes for the sols and gels, as discussed below.

After the application of a magnetic field  $\mathbf{H}$ , the magnetic moment  $\mathbf{m}$  fixed inside the particles in the sol–gel systems interact with the field via the potential

$$U_{\mathbf{m}\cdot\mathbf{H}} = -\mu_0\mathbf{m}\cdot\mathbf{H} \quad (2)$$

where  $\mu_0$  is the magnetic permeability in vacuum. As a consequence, these moments tend to align along the direction of the field by Brownian (bulk) rotation and/or Néel (magnetic vector) rotation, which lead to the apparent magnetic behavior (Shliomis & Stepanov, 1994). Because thermal motion tends to destroy alignment of the moments, the average degree of the alignment depends on the ratio of the  $\mu_0\mathbf{m}\mathbf{H}$  to thermal energy  $k_B T$ , i.e. the magnetic forces dominate the Brownian random forces (Bossis, Volkova, Lacic, & Meunier, 2002).  $\mu_0\mathbf{m}\mathbf{H}/k_B T$  is defined as the Langevin parameter  $\alpha$ , which characterizes the system under an external magnetic field (Cerdà et al., 2010). Since the magnetic moments of particles are proportional to the volume of them, the large particles can be oriented more easily than small particles. The magnetization of the  $\text{ZnFe}_2\text{O}_4$  nanoparticles is weak, so that thermal agitation has a dramatic effect on the magnetization of the sol–gel system. So, in the initial stage of magnetization ( $|\mathbf{H}| < 50$  kA/m), the susceptibility of the sol–gel systems exhibited fluctuation. Only when the absolute strength of the applied magnetic field  $\mathbf{H}$  exceeded 50 kA/m did the susceptibility curves of  $\chi$  vs.  $\mathbf{H}$  change monotonically with the magnetic field, reflecting the intrinsic effect of the interparticle interaction on the magnetization process. Therefore, discussion is focused on the field regime of  $\mathbf{H} > 50$  kA/m. For comparison, the susceptibility curves reduced by  $\phi_v$ ,  $\chi_r (=M/\phi_v H)$  vs.  $\mathbf{H}$  at  $\mathbf{H} > 50$  kA/m were measured, as shown in Figure 5. The basic considerations are believed to be the following three points:

- (1) The magnetization of the  $\text{ZnFe}_2\text{O}_4$  colloidal particles, which occurs on their surfaces, is very weak, so that the magnetic dipole–dipole interaction effect can be neglected and the apparent magnetism of the sol–gel systems results from the behavior of individual particles.
- (2) In sol–gel systems based on antimagnetic  $\text{ZnFe}_2\text{O}_4$  nanoparticles, the magnetizing mechanism is based on Brownian rotation of the moments because the local spins at the surface of the particles could be pinned (Du et al., 1987; Lodama et al., 1996) by absorbing  $\text{Fe}^{3+}$  and/or  $\text{Zn}^{2+}$  on the outer surface of the particles. This is similar to the adsorption of surfactant molecules on the surface of  $\text{Fe}_2\text{O}_3$  particles causing the spins of the iron atoms close to the surface to be pinned (Blanco-Mantecón & O’Grandy, 2006).
- (3) The colloidal particles can have a translational degree of freedom, in addition to the rotational degree of freedom that determines the magnetization behavior through Brownian rotation of the moments fixed inside the particles.

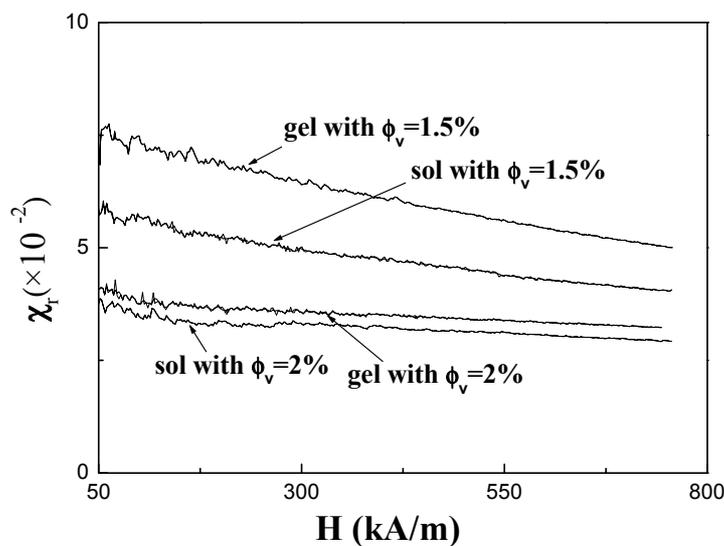


Figure 5. Susceptibility curves reduced by  $\phi_v$  at  $\mathbf{H} \geq 35$  kA/m

The results whereby the apparent magnetization or susceptibility of gels are larger than those of sols might appear to be contradictory because a computer simulation has shown that for a ferrosolid consisting of magnetic dipoles frozen at random locations but free to rotate, its susceptibility was considerably lower than for ferrofluids having fluidity (Wang, Holm, & Müller, 2002). This paradox can be explained in relation to hydrodynamic effects. A colloidal particle's motion could be influenced by another particle's motion through the carrier liquid as intermedium, which produces so-called "hydrodynamic interaction" mediated by the solvent (Zahn, Méndez-Alcaraz, & Maret, 1997). For magnetic colloids, under influence of a magnetic field, the increase of orientation of the magnetic moment of the particles leads to an increase of the effective attraction between colloidal particles, so that the randomly distributed nanoparticles in sols can tend to aggregate into chain-like structure by translational motion (Wang, Li, & Gao, 2009). Thus, in the magnetization process, a hydrodynamic interaction among the colloidal particles in a sol (Zhang et al., 1996; Bossis et al., 2002; Liu et al., 1995) could be induced through this translational degree of freedom. Experimental evidence has shown that the hydrodynamic interaction may enhance the self-diffusion of colloidal particles (Zahn et al., 1997). The diffusion coefficient  $D$  can be described as

$$D = k_B T / 3\pi\eta d \quad (3)$$

where  $\eta$  is approximately the solvent viscosity and  $d$  is the diameter of the particles (Zahn et al., 1997). Therefore, the enhancement of the diffusion is equivalent to the effective diameter of the particles becoming small. Due to the magnetic moments of particles depending on their volume, the hydrodynamic interaction makes the magnetization of the sols difficult. In inorganic gels, these colloidal particles are interlinked through van der Waals forces. Thus, after gelatinization of the sols, the translational degree of freedom can be viewed as being "frozen", but the rotational degree of freedom remains the same. Hence, the hydrodynamic interactions in a gel are negligible. Consequently, the gel is more easily magnetized than the sol, and hence the apparent susceptibility and magnetization of the former are larger than those of the latter. In addition, it can be seen from Figure 5 that the reduced susceptibility curves of the sol-gel system with  $\phi_v=2.0\%$  lie below those of the system with  $\phi_v = 1.5\%$ . This can be explained as follows.

With an increasing volume fraction of particles, the hydrodynamic interaction between the particles is enhanced accordingly since the average interparticle distance decreases. Thus the susceptibility of the sol with  $\phi_v=2.0\%$  is less than that of the sol with  $\phi_v=1.5\%$ . Also, by increasing volume fraction of particles, the viscous friction increases, which will tilt the moments of the particles against the field direction if the moments are spatially fixed in the particles (Odenbach, 2003). This effect is enhanced for the gel with  $\phi_v=2.0\%$  than for the one with  $\phi_v=1.5\%$ , and so, the susceptibility of the former is less than that of the latter.

## 5. Conclusion

For magnetic colloids with a rotational degree of freedom and a translational degree of freedom, the hydrodynamic interaction between colloidal particles, which hampers magnetization, can play an important role in the Brownian magnetization process. For the  $\text{ZnFe}_2\text{O}_4$  sol-gel system, the magnetization mechanism could be Brownian rotation of moments fixed inside particles since the moments could be pinned. Hence, the gels are different from the so-called frozen ferrofluids in the low-temperature regime, in which only Néel rotation is possible (Blanco-Mantecón et al., 2006). Gelation "freezes" the translational degree of freedom and inhibits the hydrodynamic interaction, so that the apparent susceptibility and magnetization of gels are larger than those of sols. This shows that, just as for uniaxial ferrogels, the relative rotations between the moments and the network can be viewed as a magnetic degree of freedom (Bentivegna et al., 1999) for the  $\text{ZnFe}_2\text{O}_4$  gels. In other words, the sols have a translational degree of freedom that produces a hydrodynamic interaction, but gelation will freeze this translational degree of freedom and inhibit the hydrodynamic interaction, so the gel is more easily magnetized than a sol. The action by which gelation prevents the hydrodynamic interaction effect in the magnetization process, so that the system can be more easily magnetized, may be referred to as the "gelation decoupling". The influence of the hydrodynamic interaction could be enhanced with increasing  $\phi_v$ , hence, the apparent reduced susceptibility of the sol with  $\phi_v=2.0\%$  is less than that of the system with  $\phi_v=1.5\%$ . And, increasing volume fraction of particles, the viscous friction is enhanced correspondingly, so that reduced susceptibility is lower for the gel with  $\phi_v=2.0\%$  than for one with  $\phi_v=1.5\%$ .

In addition, the hydrodynamic interaction may also be an important physical factor in making the reduced magnetization of the ferrofluids less than the magnetization of the dry particles (Chantrell et al., 1978; Berkowitz et al., 1980; Lin et al., 2010), besides producing an additional relaxation peak in the complex susceptibility of the

ferrofluids (Zhang et al., 1996). It is possible that the nanoparticles of antiferromagnetic bulk materials can form Brownian particles particularly easily. That is, so-called magnetically hard particles (Odenbach, 2009), the magnetization mechanism of which is Brownian rotation of the moments, since their moments lie on the surface of the particles and are easily pinned to form rigid dipoles, just as magnetic nanoparticles with a large anisotropy constant can be viewed as rigid dipoles (Neveu-Prin, Tourinho, Bacri, & Perzynski, 1993). Such colloids consisting of magnetic Brownian particles may exhibit special features, for example, not only an influence of the magnetic interaction on the hydrodynamic properties, but also an effect of the hydrodynamic interaction on the apparent magnetism. The latter behavior may be referred to as a “viscomagnetic effect”. Experiments have shown that compared to a ferrofluids system without magnetic interaction (i.e. in the dilution), the reduced initial susceptibility of the system with magnetic interaction is less rather than larger as theory predicts (Wang et al., 2002; Taketomi et al., 2002). The difference may be understandable with the help of the “viscomagnetic effect” resulting from the hydrodynamic interaction. In addition, this thixotropic system may have novel applications, which will be investigated further.

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