Particle blocking and carrier fluid freezing effects on the magnetic properties of Fe_3O_4-based ferrofluids

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We report the systematic dc and ac susceptibility studies on the particle blocking and carrier fluid freezing effects on the magnetization and relaxation processes in two different ferrofluids composed of Fe_3O_4 nanoparticles (mean size of ~14 nm) suspended in hexane and dodecane, which respectively have freezing temperatures below (178 K) and above (264 K) the blocking temperature of magnetic nanoparticles (~200 K). Experimental results reveal that these effects play a key role in the formation of glasslike peaks and magnetic anomalies in ferrofluids. Quantitative fits of the frequency dependent ac susceptibility to the Vogel–Fulcher model $\tau=\tau_o \exp[E_a/k(T-T_o)]$ clearly indicate that the blocking of magnetic nanoparticles in the frozen state significantly affects the interparticle dipole-dipole interaction, causing characteristic spin-glass-like dynamics. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3068461]

Ferrofluids are stable colloidal suspensions of ferromagnetic nanoparticles in a liquid carrier.[1] In the past decades, ferrofluids have been studied for potential applications in biomedicine and for other industrial applications.[2,3] The magnetic properties of ferrofluids are dominated by the dipole-dipole interaction between the suspended particles.[2,4–13] Particle size distribution,[4,5] concentration,[6,7] and surfactant coating,[8] as well as solvent used in the suspension,[9] all affect the dipole-dipole interaction, which in turn give rise to the unique range of magnetic behavior observed.[10–13] In particular, the temperature-dependent complex susceptibility ($\chi=\chi'-i\chi''$) has been noted in earlier experiments to show two characteristic peaks[11] and the zero-field-cooled (ZFC) magnetization to exhibit spin-glass-like cusp and magnetic anomaly.[13] However, understanding of the physical origin of these features in ferrofluids remained unclear in part due to the complex nature of the system and the fact that either ac susceptibility[11] or dc magnetization[13] alone was studied separately by different groups.

In this context, we have carried out systematic dc and ac susceptibility measurements on Fe_3O_4 nanoparticles in two different carrier liquids, hexane and dodecane, which are chosen to have freezing temperatures below (178 K) and above (264 K) the blocking temperature of magnetic nanoparticles (~200 K), respectively, to analyze the blocking and freezing effects on the magnetic properties of ferrofluids. The results obtained indicate that the physical origins of the observed peaks and magnetic anomalies in ferrofluids are associated with the blocking and freezing effects. The blocking of magnetic nanoparticles in the frozen state significantly affects the interparticle dipole-dipole interaction, causing characteristic spin-glass-like dynamics.

Fe_3O_4 nanoparticles were synthesized by chemical coprecipitation method described in Ref. 14. The mean particle size was ~14 nm and the particles were coated using oleic acid as surfactant. The ferrofluids were prepared by dispersing the particles in hexane and dodecane with room temperature viscosities of 0.294 and 1.35 cP, respectively. The freezing point for hexane is 178 K and 264 K for dodecane. The concentrations of both ferrofluids were ~0.02 g/ml. The crystal structure and particle sizes were determined using a Bruker D8 Focus x-ray diffractometer (XRD) and a Morgani 268D transmission electron microscope (TEM). The dc and ac magnetic characterizations were done using a commercial Physical Property Measurement System (PPMS) from Quantum Design.

In Fig. 1, we present the XRD scan of the dried ferrofluid with the peaks consistent with the cubic spinel structure of Fe_3O_4.[8] From a histogram analysis of the TEM image in the inset of Fig. 1, the average particle size was estimated as 14 ± 3 nm. This size distribution was also checked to be

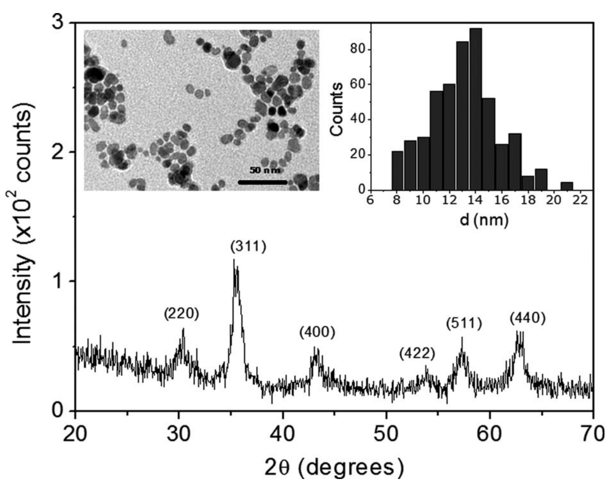

FIG. 1. Powder x-ray diffraction profile of the dried ferrofluid indexed with the (*hkl*) reflections of the cubic Fe_3O_4 phase. Upper left panel: selected area from TEM images of Fe_3O_4 nanoparticles. Upper right panel: histogram of the particle sized populations as observed from TEM images.

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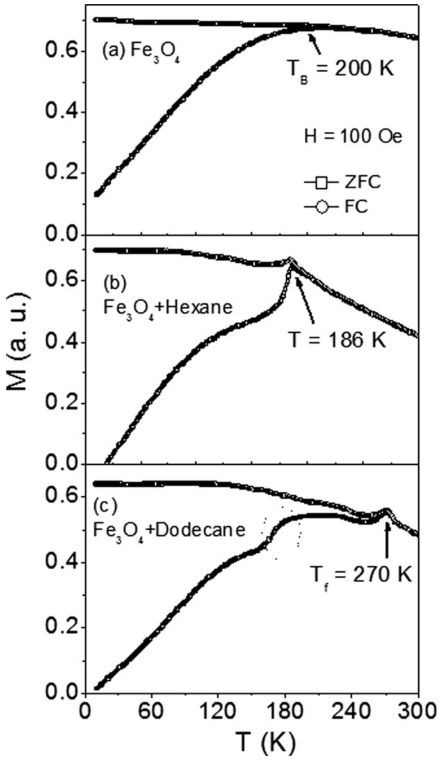

FIG. 2. ZFC-FC curves of Fe_3O_4: (a) dry powder, (b) dispersed in hexane, and (c) dispersed in dodecane.

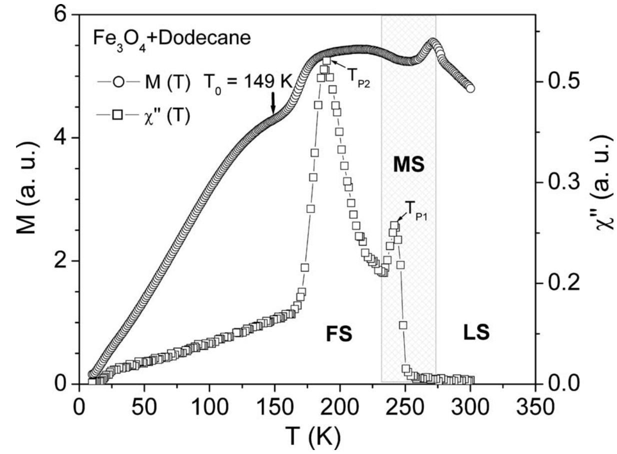

FIG. 3. Temperature dependence of ZFC magnetization and imaginary part of magnetic susceptibility χ'' of the dodecane ferrofluid. LS: liquid sate; MS: mixed state; FS: frozen state. T_o is the temperature at which the system enters a glassy state. T_{p1} and T_{p2} represent the χ'' peaks in the mixed and frozen states, respectively.

consistent with the observed blocking temperatures in the dc and ac magnetic characterizations.

Figure 2 shows the ZFC-FC dc magnetization curves for Fe_3O_4 (a) in dry powder form, (b) in hexane, and (c) in dodecane taken at an applied field of 100 Oe. The ZFC curve for powders shows a relatively broad peak at $T_B \sim 200$ K [Fig. 2(a)], which is consistent with the polydispersed nature of the magnetite nanoparticles with the associated distribution in particle size and individual anisotropy axes.[8,13,14] While the overall shapes of the ZFC and FC curves for the ferrofluids [Figs. 2(b) and 2(c)] show a similar trend, distinct cusps are seen at around 186 and 270 K. For the dodecane ferrofluid, a magnetic anomaly (i.e., the sharp jump in the ZFC magnetization at low temperature) around 181 K is also observed [Fig. 2(c)]. To understand the physical origin of the peaks and magnetic anomaly, we note that the freezing temperature ($T_F \sim 178$ K) is below the blocking temperature ($T_B \sim 200$ K) for the hexane ferrofluid [Fig. 2(b)], whereas for the dodecane ferrofluid the freezing temperature ($T_F \sim 264$ K) is much above the blocking temperature ($T_B \sim 200$ K) [Fig. 2(c)]. Therefore, the origin of the cusp at 270 K for the dodecane ferrofluid is solely associated with the freezing of the carrier liquid (dodecane, 264 K) while the cusp at 186 K for the hexane ferrofluid results from both the carrier liquid freezing and particle blocking effects. The presence of magnetic anomaly around 181 K for the dodecane ferrofluid is due to the blocking effect of magnetic nanoparticles that occurs near this temperature. Since the freezing of the carrier liquid abruptly stops the physical motion of the nanoparticles and alignment of moments in the field direction, the cusps at 186 and 270 K [Figs. 2(b) and 2(c)] are sharper compared with that at 200 K [Fig. 2(a)] relating to the blocking mechanism of the spins within the nanoparticles, which is due to a competition between thermal energy (k_BT) and anisotropy energy (KV). As compared with the dodecane ferrofluid, the cusp at 186 K for the hexane ferrofluid [Fig. 2(b)] is more pronounced because both the freezing and blocking mechanisms contribute to it.

We now attempt to correlate the physical origin of the two peaks in the ac complex susceptibility[11] to the peak and magnetic anomaly in the ZFC dc magnetization.[13] For this purpose, we carried out ac susceptibility measurements on the dodecane ferrofluid which shows the glasslike peak ($\sim$270 K) and magnetic anomaly ($\sim$181 K) in the ZFC magnetization. Similar to the features reported in Ref. 11, we have also observed the two characteristic relaxation peaks in $\chi''(T)$ for the dodecane ferrofluid. As demonstrated by Zhang *et al.*,[11] there exist three characteristic states (e.g., liquid, mixed, and frozen states) in a ferrofluid or solvent. For temperatures above the pour point (T_{pour}) a *liquid* phase exists as the system flows like a fluid, whereas a *solid* phase (or a frozen state) is present at low temperatures below $T_{s\text{-}m}$, and a *mixed* phase exists in the temperature range between $T_{s\text{-}m}$ and T_{pour}, where $T_{s\text{-}m}$ is the transition temperature from the solid phase to the mixed phase. Importantly, the first peak in χ'' (at high temperature) has been found to belong to the temperature range of $T_{s\text{-}m} < T < T_{pour}$ (in the mixed state) while the second peak in χ'' (at low temperature) to the frozen state.[11]

In the present study, the excellent correlation between the features in the dc and ac magnetizations for the dodecane ferrofluid is best revealed in the combined plots shown in Fig. 3, from which one can infer that the second peak in $\chi''(T)$ is ascribed to the blocking of magnetic nanoparticles, while the first peak in $\chi''(T)$ is associated with the freezing of the solvent. As one can also see clearly from Fig. 3, the first peak reflects the magnetic behavior in the mixed state, while the second peak represents the magnetic behavior in the frozen state. This important finding allows us to correctly classify the two peaks in $\chi''(T)$ (the peak and magnetic anomaly) as due to freezing and blocking for Fe_3O_4 ferrofluids with

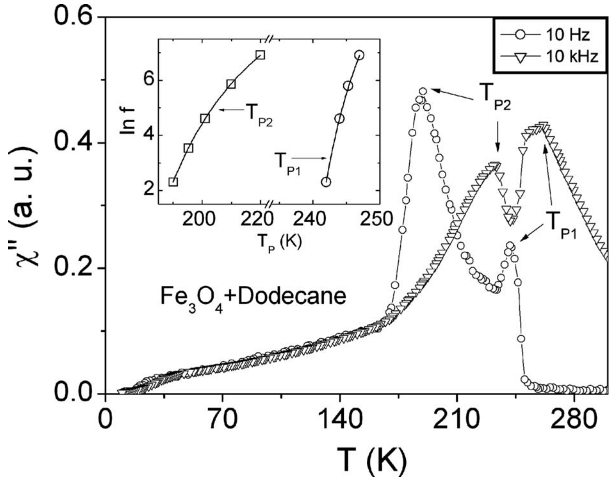

FIG. 4. Temperature dependence of the imaginary part of susceptibility χ'' of the dodecane ferrofluid at two representative frequencies of 10 Hz and 10 kHz. The inset shows the best fits of $T_p(f)$ data to the VF model extracted from ac susceptibility of the dodecane ferrofluid.

kerosene solvent reported in Ref. 11 and for Fe_3O_4 ferrofluids with hexane solvent reported in Ref. 13.

Apart from this, we note that the peaks in $\chi''(T)$ shift to higher temperatures as the measurement frequency is increased (Fig. 4), indicative of glassy behavior.[15] The glassy nature in ferrofluids is reasonably complex as contribution to the glassy states in the mixed and frozen regions results from the combined blocking and freezing effects.[10,13,16] To clarify the blocking and freezing effects on the glassy behaviors in the mixed and frozen sates, we analyze the frequency dependence of the peaks of $\chi''(T)$ by fitting the data using the Néel–Arrhenius model

$$\tau = \tau_o \exp(E_a/kT) \tag{1}$$

and Vogel–Fulcher (VF) scaling law

$$\tau = \tau_o \exp[E_a/k(T-T_o)], \tag{2}$$

where τ is the relaxation time ($\tau=1/f$; f is the frequency), τ_o is the microscopic flipping time of the fluctuating spins, E_a is the thermal activation energy, T is the temperature, and T_o is the characteristic temperature with thermal energy dominating for $T>T_o$ and interaction energy for $T<T_o$.

Our results reveal that the $\chi''(T)$ data can be fit using Eq. (1), but the fitting parameters obtained are unphysical, similar to the case reported earlier in Ref. 11. This suggests that these ferrofluids belong to the class of interacting particle systems for which the Néel–Arrhenius model is invalid. For our dodecane ferrofluids, the VF model [e.g., Eq. (2)] has been found to fit well the $\chi''(T)$ data with acceptable fit parameters, and the results are shown in the inset of Fig. 4. The best fits yield $\tau_o=(1\pm0.3)\times10^{-7}$ s, $E_a/k=(1.4\pm0.5)\times10^2$ K, and $T_o=232$ K for the case of the first peak (T_{p1}) and $\tau_o=(1.8\pm0.4)\times10^{-6}$ s, $E_a/k=(4.5\pm0.4)\times10^2$ K, and $T_o=149$ K for the case of the second peak (T_{p2}) with an error of ±1 K for T_o. The difference in τ_o and E_a/k for the cases of T_{p1} and T_{p2} indicates that for the ferrofluid having $T_B<T_F$, the glassy behavior is different in nature between the mixed and frozen states. This is understandable as the magnetic particles are unblocked in the former case, whereas they are already blocked in the latter case. The larger values of τ_o and E_a/k for the case of T_{p2} indicate that the blocking effect of magnetic nanoparticles on the glassy behavior in the frozen state is simply to cause slowing down of the dynamics of the system. In addition, we find that $T_o=232$ K for the case of T_{p1}, which coincides with the temperature at which the ferrofluid enters into the frozen state from the mixed state, and this transition is the origin of the divergence in the viscosity of the ferrofluid, whereas the divergence of the relaxation time at $T_o=149$ K for the case of T_{p2} suggests that the system enters a glassy state at this temperature. In view of these results, we propose that the blocking of magnetic nanoparticles in the frozen state significantly affects the interparticle dipole-dipole interaction, causing characteristic spin-glass-like dynamics. This allows one to reconcile the observations of spin-glass-like states, magnetic relaxation, and aging effect reported in the literature for ferrofluids.[10,13,16]

In summary, we have demonstrated that the particle blocking and carrier liquid freezing effects are important for the formation of the spin-glass-like peaks and magnetic anomalies in ferrofluids. In the frozen state, the blocking of magnetic nanoparticles significantly affects the interparticle dipole-dipole interaction, causing characteristic spin-glass-like dynamics. Further work is in progress to investigate the particle blocking effect on the liquid state and attempt to establish a correlation between the blocking temperature of magnetic nanoparticles and the freezing temperature of the solvent in ferrofluids.

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