Effects of surfactant friction on Brownian magnetic relaxation in nanoparticle ferrofluids

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Measurement of the variation of relaxation frequency of Brownian rotation of magnetic nanoparticles in a ferrofluid due to binding of organic molecules is a possible tool for detection of biomolecules in solution. We investigate frequency- and temperature-dependent magnetic behavior of model ferro-fluids of surfactant-coated Co nanoparticles, 20 nm in diameter, in dichlorobenzene in a wide concentration range. At room temperature the most diluted ferrofluids have a single relaxation frequency determined by the fluid viscosity and effective particle volume. Increasing concentration leads to an appearance of the second, low-frequency relaxation peak, attributed to the effective viscosity associated with interparticle friction. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855195]

Application of nano- or microsized magnetic particles in biomedical area has been intensively studied, and several techniques utilizing magnetic particles in magnetic separation, drug delivery, and imaging have been proposed.[1] One of the suggestions is based on the possibility of selectively attaching biological molecules to nanoparticles[1] for further recognition. Detection of the magnetically labeled biological entities can then be performed with on-chip magnetic sensors, such as giant magnetoresistance,[2] spin valve,[3] Hall-effect[4] or planar Hall-effect[5] sensors, by measuring the stray fields of particles in their vicinity. Alternatively, it has been proposed to measure and analyze the Brownian relaxation of magnetic particles, with attached biomolecules, suspended in a ferrofluid. The Brownian relaxation time τ_r depends on the effective particle hydrodynamic radius r, $\tau_r = 4\pi r^3 \eta / k_B T$ (η is the viscosity). Binding of organic molecules to the particles changes the effective particle volume, and the resulting increase of relaxation time can be utilized for recognition of these biomolecules.[6] This method has been experimentally verified recently[7] by measurements of the frequency dispersion of ac susceptibility in a ferrofluid containing magnetic nanoparticles with and without bound biomolecules. The resulting shift of the relaxation frequency has been interpreted within a model which neglects interaction between biomolecule-coated magnetic nanoparticles. However, in a concentrated solution these interactions (magnetic and van der Waals) cannot be neglected. Moreover, since the Néel rotation of the moment[8] needs to be blocked to make the Brownian relaxation dominant, magnetic forces will lead to long-range interactions and possibly aggregation even in a diluted ferrofluid. Thus interparticle interactions must contribute to relaxation. In this paper we report detailed investigation of this effect using a model ferrofluid containing 20-nm Co nanoparticles coated with oleic acid. It is shown that at a close distance between particles surfactant friction leads to relaxation with characteristic frequency much lower than

that in a diluted solution. For the biomedical application, while complicating the standard analyses, this additional relaxation can be useful for recognition of the bound biomolecules, as it contains information on their mechanical properties.

We investigated the magnetic behavior of model ferrofluids of surfactant-coated Co nanoparticles, 20 nm in diameter, in dichlorobenzene. Nanoparticles were synthesized by a modified La Mer method[9–11] involving the injection of organometallic precursors into a hot coordinating solvent containing a surfactant (oleic acid), under inert atmosphere. The synthesis includes homogeneous nucleation followed by growth to a desired size in the solution. The surfactant dynamically coats the particles in the process. The crystal structure of the Co nanocrystals has been investigated by x-ray and electron diffraction, and their arrays have been observed by high-resolution electron microscopy.[10,11] Figure 1 shows a transmission electron microscopy (TEM) image of 20-nm particles deposited on a TEM grid. The length of surfactant molecule is about 1.5 nm. Particles form chains due to magnetic interactions,[9,10] as the individual particles are ferromagnetic at room temperature. The estimated magnetic moment per particle is about 6×10^{-18} J/T.
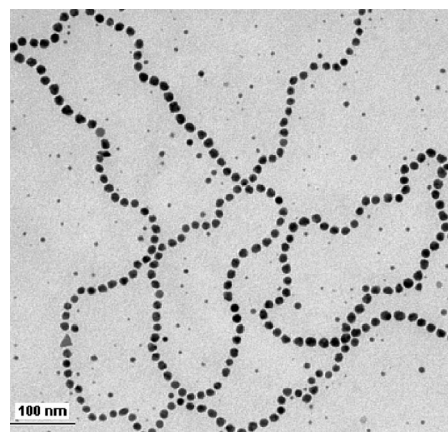

FIG. 1. TEM image of 20-nm Co nanoparticles deposited on a TEM grid.

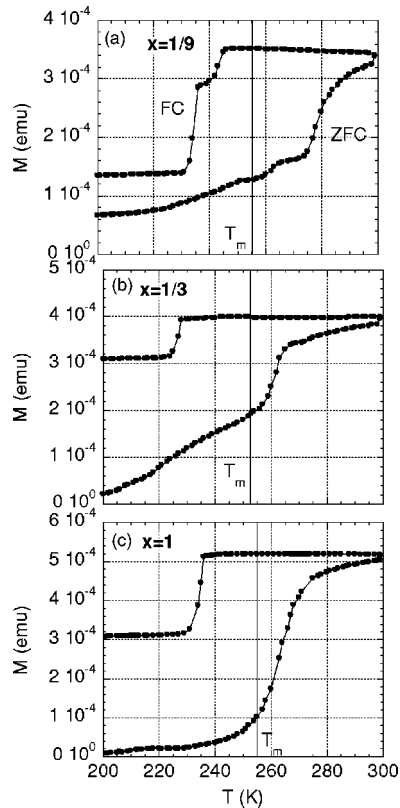[a]Author to whom correspondence should be addressed; electronic mail: kannanmk@u.washington.edu

FIG. 2. Zero-field cooled and field cooled magnetization measurements in a dc field of 10 Oe on ferrofluids with concentrations $x=$ (a) 1/9, (b) 1/3, and (c) 1. T_m is the melting point of the solvent

FIG. 3. Real (open symbols) and imaginary (filled symbols) moments as a function of frequency in samples with different magnetic volume fraction x. The measurements were made at 300 K (circles), at 250 K after warming from 200 K (squares), and at 250 K after cooling from 300 K (triangles). Excitation field is 4 Oe.

Ferrofluids were prepared by dissolving nanoparticles in dichlorobenzene, followed by shaking and sonication. We first prepared a "concentrated" suspension by adding particles until visible aggregation and sedimentation started. In this work the magnetic volume fraction corresponding to concentrated ferrofluid is denoted as $x=1$. By adding more solvent ferrofluids with $x=1/3$, 1/9 and 1/27 were obtained. The solutions were sonicated before measurements to keep particles suspended in the fluid. The highest concentration achieved ($x=1$) corresponds to less than 0.1% Co metal by volume, based on measurements of saturated moment. Both dc and ac (0.01–1000 Hz) magnetic measurements were performed on a Quantum Design magnetic properties measurement system (MPMS). Zero-field cooled and field cooled (ZFC-FC) dc magnetization in applied field of 10 Oe and the complex ac susceptibility with the drive amplitude of 4 Oe were measured as a function of temperature and frequency in a temperature range of 200–300 K. All the data presented are for 0.2 mL of fluid in a Teflon container. For the chosen particle size, the blocking temperature is much above 300 K, hence magnetic relaxation is determined by the Brownian rotational diffusion.

Figure 2 shows ZFC-FC magnetization measurements on samples with concentrations $x=1/9$, 1/3, and 1. $T_m \sim 255$ K is the handbook value for the solvent melting point. The temperature dependences show complex behavior with thermal hysteresis, related to undercooling and overheating. It is interesting that slowing down the temperature rate does not remove the hysteresis. We notice that for diluted ferro-
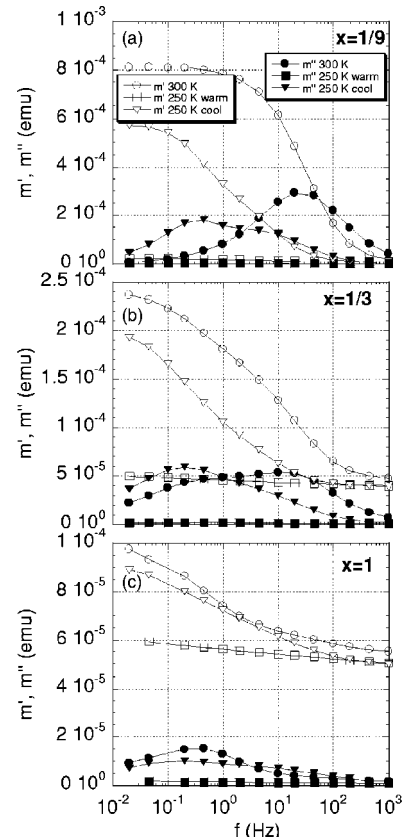
fluids both melting and freezing are two-step processes, while these steps are not seen in concentrated ferrofluids. The temperature dependences of ac susceptibility measured at different frequencies (not shown here for brevity) follow, in general, similar trends with thermal hysteresis.

Figure 3 shows frequency dependences of both the real (open symbols) and imaginary (filled symbols) parts of ac moment for the same samples at $T=300$ K and $T=250$ K. Due to thermal hysteresis, the results at 250 K are different for the sample cooled down from 300 K and warmed up from 200 K. In the latter case the rotational degree of freedom remains frozen, and susceptibility is very small. The most striking feature seen in these plots is the coexistence of two relaxation processes in the system resulting in two distinct maxima of the imaginary part of susceptibility, one at about $f_{rH} \sim 20$–50 Hz (high-frequency peak), and the other at $f_{rL} \sim 0.2$–0.5 Hz (low frequency peak). At 300 K, the high-frequency process is dominant in the diluted ferrofluid, while the low-frequency process dominates the behavior of the concentrated solution. At intermediate concentration, both relaxation peaks are clearly recognized. At 250 K (upon cooling from high temperature) the low-temperature peak increases also in diluted systems. In order to clarify the origin of the low-frequency peak we performed measurements on diluted ferrofluids with $x=1/27$ 10 days after the ferrofluid was prepared. The frequency dispersion of susceptibility of a freshly prepared sample was similar to that of $x=1/9$ [Fig.
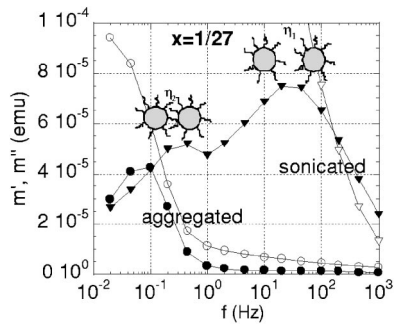
FIG. 4. Dispersion in 10 days old aggregated solution with $x = 1/27$, and the same ferrofluid after a 15-s sonication. Situations responsible for the two peaks of m'' are presented in the cartoons.

3(a)]. In 10 days particles were visibly aggregated and sedimented at the bottom of the container. Measurements resulted in a single peak at a frequency below 0.1 Hz. (Fig. 4, circles). Sonication for 15 s led to a double-peak characteristic with $f_{rH} \sim 20$–50 Hz and $f_{rL} \sim 0.2$–0.5 Hz, shown by the triangles in Fig. 4, while further sonication and shaking led to complete disappearance of the low-frequency peak (not shown in the figure).

While it is logical to attribute the high-frequency peak in ac susceptibility at f_{rH} (Figs. 3 and 4) to the Brownian relaxation of isolated nanoparticles, modified by the effective increase of hydrodynamic volume due to surfactant, the low-frequency anomaly requires additional consideration. The low-frequency peak appears either at high concentration of particles in the uniform ferrofluid, or in a diluted, but not mixed well, solution. Apparently interparticle interaction plays a role. Magnetic dipole-dipole interactions can lead to an effective increase of magnetic volume[12] and hence a decrease in the relaxation frequency. However, in this case the two peaks would not coexist in a uniform solution, as seen in Fig. 3(b). A double loss peak has been observed in a ferrofluid in Ref. 13, and the low-frequency peak has been attributed to the rotational diffusion of aggregates of nanoparticles with effective volume larger than the volume of the single particles. This interpretation was extended in Ref. 14, where estimated relaxation frequencies of chain fragments were found in agreement with cryo-TEM observations on some samples. In the approximation used in Ref. 14 (see Fig. 11 there), our experimental result $f_{rH}/f_{rL} \sim 40$–100 would require the existence of chains of nanoparticles in the solution consisting of about 5–7 nanoparticles to provide the observed low-frequency relaxation peak. However, we have not found such aggregates in the available TEM images (see Fig. 1). It is seen that most of nanoparticles are aggregated in much longer chains. At present we do not have any evidence of the existence of short chains of nanoparticles of selected length which would confirm the above model. Alternatively, we suggest that the peak at f_{rL} is due to friction between surfactant layers on the surface of the particles which appear to be close to each other in the ferrofluid. The low relaxation frequency is about two orders of magnitude (a factor

~40–100) lower than the high one, meaning that the effective viscosity associated with interparticle friction is two orders of magnitude higher than the solvent viscosity. In the first approximation, we can compare this ratio with the ratio of viscosities $\eta_{OA}/\eta_{DCB} \sim 20$, where $\eta_{DCB} \sim 1.32$ mPa s and $\eta_{OA} \sim 27.64$ mPa s are the viscosities of oleic acid and 1,2-diclorobenzene. This seems a good qualitative fit for this crude model. In Fig. 4, we show cartoons of the two situations, or relaxation processes, resulting in the low-frequency and high-frequency peaks. We notice that if this model were to be correct, measurement of the low-frequency peak can give additional information on the origin of the organic molecules attached to particle surface. Indeed, its position depends not only on the effective volume of the particle with surfactant, but also on the mechanical properties of (flexibility) and interaction between the molecules. It may hence be developed into a more detailed method of biomolecule recognition. Experimental studies are being planned to develop the physics of the double-peak relaxation behavior of ferrofluids more clearly.

In conclusion, we have presented a detailed study of susceptibility of suspensions of ferromagnetic nanoparticles coated with organic molecules imitating biomolecules. Our results confirm applicability of ac relaxation measurements for biosensing. In addition to the relaxation determined by the solvent viscosity and effective single-particle volume, we observe a low-frequency relaxation process. We attribute it to surface friction of surfactant on neighboring particles. This provides additional opportunities for biomolecule recognition.

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