JOURNAL OF APPLIED PHYSICS **99**, 08H107 (2006)

Brownian magnetic relaxation of water-based cobalt nanoparticle ferrofluids

Y. Bao, A. B. Pakhomov, and Kannan M. Krishnan[a)]
Materials Science and Engineering, University of Washington, Seattle, Washington 98195-2120

(Presented on 1 November 2005; published online 5 May 2006)

Following the synthesis of monodispersed 20 nm cobalt nanoparticles via a thermal decomposition method we have successfully transferred these hydrophobic nanoparticles into the water phase using tetramethylamonium hydroxide pentahydrate as phase transfer agent and 12-aminododecanoic acid as a stabilizing agent. Frequency dependent ac susceptibility of water-based cobalt nanoparticle ferrofluids was measured at room temperature in the frequency range of 0.01–1000 Hz. In addition to the "high" frequency magnetic relaxation peak at 200 Hz, which is determined by the solvent viscosity and hydrodynamic volume of the nanoparticles, a lower frequency relaxation peak attributed to the interaction of surface coatings is observed. The position of the latter varies with the solution *p*H in the range of 0.02–0.05 Hz. This variation is explained as due to the change of chemical and charge state of the surfactant molecules. The peak at low frequency may be potentially used to study protein configuration changes in solution or other dynamic properties of biomolecules. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2172203]

Magnetic nanoparticles have been used in a wide range of biological and medical applications which utilize various magnetic properties.[1] For example, magnetic separation and drug delivery utilize the manipulation of magnetic nanoparticles with magnetic field gradients; Néel relaxation of superparamagnetic nanoparticles in an ac magnetic field is explored for magnetic hyperthermia and in magnetic resonance imaging (MRI), the magnetostatic stray field generated by the particles can affect the relaxation of protons thus providing contrast in MRI. Recently, dynamic properties of magnetic nanoparticles have been intensively studied because of their great potential in biological sensing. For example, magnetic immunoassay has been developed to detect and qualify specific biological targets. The key point is that magnetic nanoparticles bound to specific targets can be distinguished from unbound ones by their different relaxation times. When the magnetic nanoparticles are immobilized, the Brownian relaxation is suppressed. Thus this technique provides a quantitative measure of the amount of bound molecules.[2] Alternatively, it has been proposed to measure and analyze the Brownian relaxation of magnetic nanoparticles coated with surface coating in solution. The Brownian relaxation time τ depends on the effective particle hydrodynamic volume, $\tau = 3V_H\eta/k_BT$ (V_H is the particle hydrodynamic volume and η is the viscosity of the solution). Any surface coating change which affects the particle hydrodynamic volume will result in a change of relaxation time, which can be used to detect binding or other dynamic events.[3] This method has been experimentally verified by measuring the frequency dependent ac susceptibility of magnetite nanoparticles in solution.[4]

Our previous studies of ferromagnetic cobalt nanoparticles *in organic solution* have shown that for a concentrated solution, friction between the particle surface coating leads to an *additional* relaxation peak with characteristic frequency much lower than that for isolated particles. This additional relaxation was proposed as a tool for the recognition of binding molecules, study of the interaction behaviors, and mechanical properties of surface coating on ferromagnetic nanoparticles.[5] However, for practical applications in biomedicine, it is important to demonstrate that this approach is useful for aqueous ferrofluids. In this paper, this method is demonstrated in a study of surfactant interaction effects on the low frequency peak in *aqueous* solutions of 20-nm-diameter cobalt nanoparticles. It is shown that changing of *p*H effectively controls surfactant interactions and provides a model system with variable peak frequency.

We investigated the magnetic behavior of 20-nm-diameter cobalt in water-based ferrofluids in ac magnetic field. Cobalt nanoparticles were synthesized via thermal decomposition of cobalt carbonyl in the presence of surfactant at high temperature under inert atmosphere.[6] These particles can be precipitated out from the original organic solution [1,2-dichlorobenzene (DCB)] by adding excess methanol followed by centrifugation. The precipitated particles can be redispersed in water phase using tetramethylamonium hydroxide pentahydrate (TMAOHP) as a phase transfer agent and 12-aminododecanoic acid (12-AA) as a stabilizing agent. TMAOHP water solution is prepared by adding TMAOHP solid in de-ionized water until *p*H of the solution is about 9–10. Redispersion of cobalt nanoparticles in water requires the removal of the original surface coating, tri-*n*-octylphosphine oxide (TOPO) and subsequent replacement with negative hydroxide ions, which is in turn surrounded by the positive tetramethylammonium conterions, forming a double layer connected by ionic interactions.[7] This method has been used to transfer other magnetic nanoparticles from organic phase into aqueous phase, such as magnetite[8] and FePt.[9] However, in our case, the tetramethylammonium counterions do not provide strong enough repulsion between

---

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

0021-8979/2006/99(8)/08H107/3/$23.00

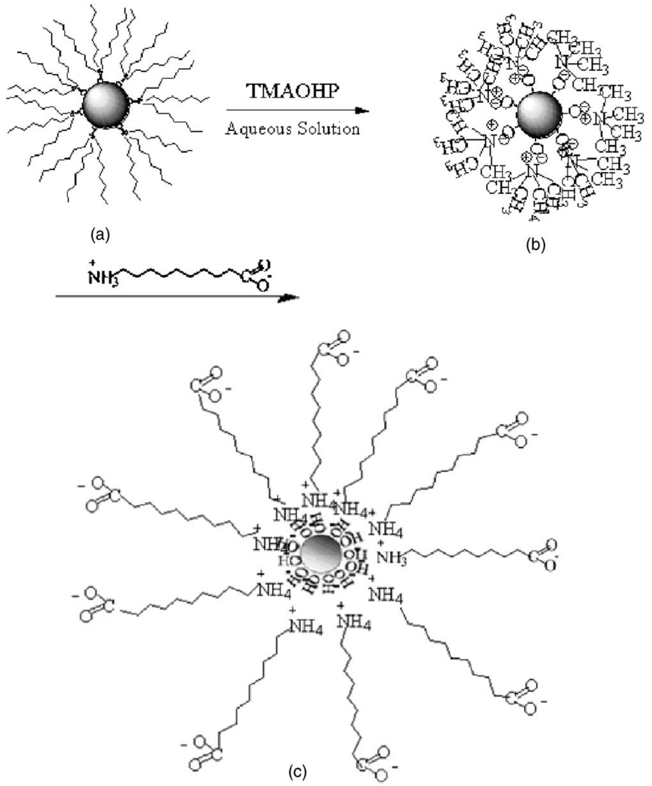

FIG. 1. Preparation sequence of water-based cobalt nanoparticle (a) TOPO coated cobalt nanoparticles and (b) TMAOHP coated cobalt nanoparticles by the charged double layer. (c) 12AA stabilizer coated cobalt nanoparticles.

the ferromagnetic cobalt nanoparticles; particles tend to aggregate after a few hours. Therefore, 12-AA stabilizer is added to make stable water suspension of cobalt nanoparticles. In a basic solution, 12AA exists in a form with a negatively charged–COO^- group at one end and positively charged–NH_3^+ ions at the other end by internal proton transfer. These positively charged ends of 12AA surfactants can substitute the tetramethylammonium counterions and form a layer of 12AA surfactant with–COO^- groups sticking out from the nanoparticle surface. The whole process can be described with a cartoon in Fig. 1. Further these 12AA stabilized cobalt nanoparticles are dispersed in phosphate buffered saline (PBS) solution with three different *p*H values (5, 7, and 9) to make saturated PBS solution for further magnetic measurements. Here, the ionic strength of PBS solution is about $0.015M$ at *p*H around 7.0, and further the hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the *p*H to desired value. In the acidic solution, two possible surface environments could happen—either the negatively charged–COO^- is neutralized to form—COOH or a positively charged complex H_3O^+ is attached to–COO^-—whereas in the basic solutions the dangling ends of surfactant molecules are negatively charged. This could serve as a model to study the surface coating frictions by varying the ionic forms of the surface groups.

Figure 2 shows the transmission electron microscopy (TEM) images of nanoparticle samples prepared from (a) 1,2-diclorobenzene-based and (b) 12AA stabilized water-based ferrofluids. The main difference between these two images is that organically capped cobalt nanoparticles in nonpolar solution form chains on the TEM grid due to the magnetic interaction,[10] while the disordered arrangement of nanoparticles is observed for water-based solution. The latter is probably due to competing forces of magnetic interaction and ionic repulsion. This also confirms the change of surface coating after surface modification.

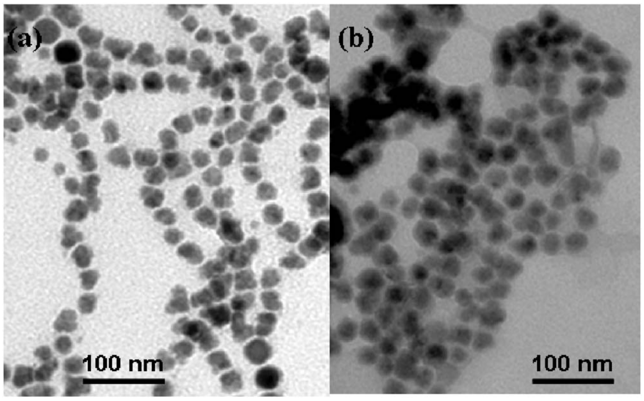

FIG. 2. TEM images of 20 nm cobalt nanoparticles deposited on TEM grid from (a) organic (DCB) solution (b) aqueous solution.

Cobalt saturated water-based solution is prepared by adding particles into TMAOHP water solution followed by sonication until visible sedimentation starts. The top solution is then used for magnetic measurements. Cobalt nanoparticles in TMAOHP+12AA in PBS at *p*H 5, 7, and 9 are prepared in a similar way. These saturated cobalt solutions contain less than 0.1% cobalt metal by volume based on the measurements of saturation magnetic moment. ac magnetic measurements were performed on a Quantum Design magnetic properties measurement system (MPMS). Complex ac susceptibility was measured as a function of frequency with a drive amplitude of 4 Oe in a frequency range of 0.01–1000 Hz. The standard deviations of both the real and imaginary parts of the moment were $\lesssim 10^{-7}$ emu at all frequencies. The moment values were normalized to the volume of cobalt in the ferrofluid, calculated based on the measured saturation moment. For the chosen particle size, the blocking temperature is much higher than 300 K in the whole frequency range; hence magnetic relaxation is determined by the Brownian relaxation mechanism.

Figure 3 shows the frequency dependences of both the real and imaginary parts of ac moments for the nanoparticles coated with surfactant in aqueous solutions of variable *p*H at 300 K. The behavior of ac susceptibility is qualitatively similar to that observed before in ferrofluids based on DCB.[5] The imaginary part of the susceptibility has two well-defined peaks. The position of the high frequency peak at about 200 Hz is independent of the solution acidity. This maximum is determined by the relaxation frequency of isolated particles in the solvent: $f_{rH}=k_BT/\eta V_H$, where V_H is the hydrodynamic volume of nanoparticles, including the surface organic coatings and other adjacent layers. The average distance between these isolated particles can be estimated from the measured Co volume fraction and particle size to be on the order of 100 nm. Contribution from interparticle interaction, including steric and Coulomb, is negligible at these distances.

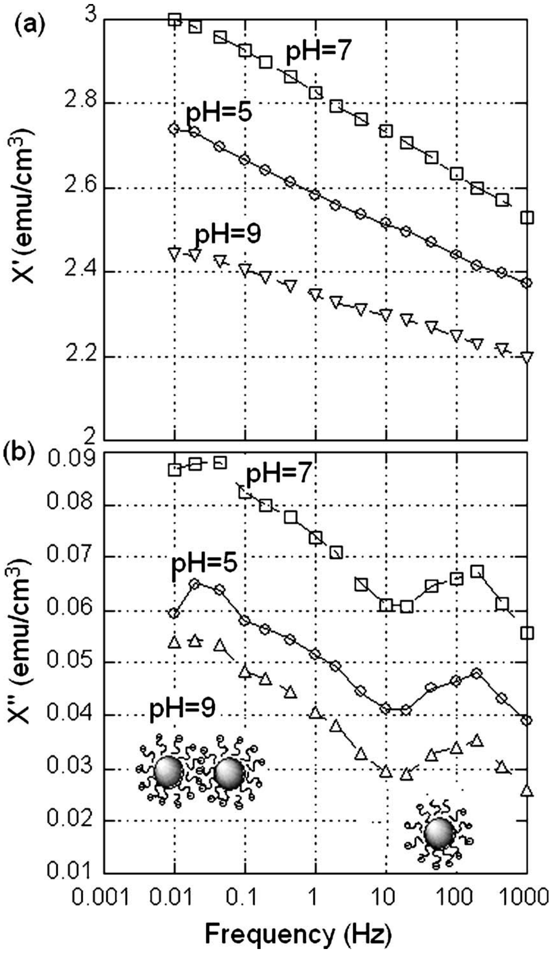

FIG. 3. Frequency dependences of the complex moment for surfactant-coated Co nanoparticles in water-based solutions with pH=5 (circles), 7 (squares), and 9 (triangles). (a) Real part of the moment and (b) imaginary part of the moment. The insets show the cartoons of the two situations, or relaxation processes, resulting in the low frequency and high frequency peaks in a basic solution. Moments are normalized to the volume of Co metal in the solution which is estimated from saturated magnetic moment. The standard deviation of the measured values is $\lesssim 10^{-3}$ emu/cm^3 of Co, smaller than the symbol size.

The low frequency peak position is dependent on the different pH environments, with the relaxation frequency being the highest ($f_{rL} \sim 0.05$ Hz) in the neutral solution. In the acidic solution the lower relaxation frequency decreases to $f_{rL} \sim 0.02$ Hz. The change in the base solution is less pronounced; however, the maximum also appears to be at a frequency lower than 0.05 Hz. According to the model developed before,[5] the low relaxation frequency is determined by effective interactions between the surfactant molecules on aggregated fraction of particles, leading to an additional surface friction, appreciably stronger than that for an isolated particle suspended in the solvent. Particle aggregation is dominated by the magnetic attractive forces in our case. It follows from the data in Fig. 3 that both $p\mathrm{H} < 7$ and $p\mathrm{H} > 7$ lead to the enhancement of interactions between surfactant chains and hence a decrease in the low relaxation frequency. For an acidic solution, it is possible that hydrogen bonding increases the friction of the surfactant chains. In a basic solution, the particle has a negatively charged surface due to the–COO$^-$ groups. For a qualitative explanation of the increase of friction in this case, consider two nanoparticles closely drawn together by magnetic attraction forces as shown in the left cartoon in Fig. 3(b). The steric forces increase with decreasing distance, the latter being determined by the balance between magnetic attraction and repulsion due to the screened Coulomb potential. The ionic strength I of PBS buffer solution at pH=9 (I=0.029M) is larger than that at pH=7 (I=0.015), because NaOH is added to adjust the pH value. Hence the Debye screening length[11] decreases from 2.42 nm at pH=7 to 1.81 nm at pH=9, making the repulsion more short ranged and leading to a decrease in interparticle distance and an increase in the friction between neighboring particles. Therefore, a relatively lower relaxation frequency is observed.

Variation of the solution acidity is used in this work to control interactions (friction) between surfactants on neighboring Co nanoparticles within particle aggregates in water-based ferrofluids, while maintaining constant effective hydrodynamic volume of the particles and constant fluid viscosity. Hence this variation affects the low frequency behavior of susceptibility but does not change the magnetic response at high frequency. These results demonstrate the applicability of monitoring the low frequency anomaly associated with interparticle friction for identification of the properties of surfactant other than just the length of surfactant chains. This measurement is potentially more informative for identification of biomolecules in the solution than monitoring the high frequency peak. In particular, this peak at lower frequency may be used to study protein configuration change with solution environments since protein configuration changes when they are immobilized on the substrates or other surfaces. Further, other dynamic properties of biomolecules in solution may be probed with this method as well.

This work is funded by NSF (DMR-0501421) and the Campbell Endowment at UW.

[1] Q. A. Pankhurst, J. Connolly, S. K. Jones, and J. Dobson, J. Phys. D **36**, R167 (2003).

[2] W. Weitschies, R. Kötitz, T. Bunte, and L. Trahms, Pharm. Pharmacol. Lett. **7**, 1 (1997).

[3] J. Connolly and T. G. St. Pierre, J. Magn. Magn. Mater. **225**, 156 (2001).

[4] S. H. Chung, A. Hoffman, S. D. Bader, L. Chen, C. Liu, B. Kay, and L. Makowski, Appl. Phys. Lett. **85**, 2971 (2004).

[5] A. B. Pakhomov, Y. Bao, and K. M. Krishnan, J. Appl. Phys. **97**, 10Q305 (2005).

[6] 1.58 mmol (0.54 g) of cobalt carbonyl dissolved in 3 ml DCB was injected into DCB (182 °C) containing 0.26 mmol (0.1 g) trioctylphosphine oxide (TOPO), and refluxed for 45 min and then aging for 15 min at lower temperature (140 °C).

[7] R. Massart, IEEE Trans. Magn. **17**, 1247 (1981).

[8] L. E. Euliss, S. G. Grancharov, S. O'Brien, T. J. Deming, G. D. Stucky, C. B. Murray, and G. A. Held, Nano Lett. **3**, 1489 (2003).

[9] V. Salgueiriño-Marceira, L. M. Liz-Marzán, and M. Farle, Langmuir **20**, 6946 (2004).

[10] Y. Bao, M. Beerman, and K. M. Krishnan, J. Magn. Magn. Mater. **266**, L245 (2003).

[11] R. J. Hunter, *Introduction to Modern Colloid Science* (Oxford University Press, New York, 1993).