Thermal Motion of Magnetic Iron Nanoparticles in a Frozen Solvent

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The thermal rotation of iron nanoparticles dispersed in cyclohexane was studied by measuring the dynamic magnetic susceptibility above and below the freezing point of the solvent. Above the freezing point, the orientation of the magnetic dipoles changes mainly by reorientation of the entire particle. Below the freezing point, complete arrest of particle motion was expected, such that the magnetic dipoles would only be able to reorient themselves inside the nanoparticles (Néel relaxation). However, we find that thermal motion continues well below the temperature at which the bulk of the solvent is frozen. We ascribe this to local lowering of the freezing point, due to the presence of polymers in the close vicinity of the colloids. Furthermore, because strong dipole−dipole interactions result in the formation of dipolar chains, we have systematically studied the effect of particle size on dynamics in a frozen solvent. For the larger particles, our data indicate that local wiggling of the individual particles in a chain may become the dominating mode of thermal motion.

Introduction

Ferrofluids are colloidal dispersions of magnetic single domain particles and are convenient model systems to explore fundamental issues in dipolar fluids.[1−3] The dipolar interactions can be studied experimentally using magnetic techniques. In several studies ferrofluids have been frozen, yielding a system of immobile particles randomly distributed in three dimensions with the dipoles relaxing by the Néel mechanism.[4−7] The underlying assumption is that the motion of the particles is switched off in a frozen solvent.

The dominant magnetic relaxation mechanism in a ferrofluid is either Néel or Brownian rotation, depending on the time scale on which each of these processes takes place. When relaxation is dominated by Brownian rotation, the magnetic moment can be considered as blocked within the particle. Reorientation of the magnetic dipole in an applied magnetic field then occurs by rotation of the entire particle. At temperatures far below the freezing point of the solvent, the particles are presumably immobilized and, consequently, relaxation of the magnetic moment occurs by rotation of the dipole within the particles (Néel relaxation). Experimentally, the rotation rate of magnetic dipoles can be studied by measuring the dynamic susceptibility.[8−10] This also allows detection of aggregates, because they substantially slow the magnetic relaxation.

In this paper, we report dynamic susceptibility measurements on frozen ferrofluids. Using different iron dispersions with particles of well-determined size,[11] we have systematically studied the effect of increasing dipole−dipole interactions. It was recently demonstrated that dipole−dipole interactions in these iron dispersions may be sufficiently strong to lead to the formation of dipolar chains.[12] The initial plan here was to study Néel relaxation in immobilized particles by measuring the dynamic susceptibility in frozen ferrofluids. However, we found that the magnetic susceptibility of our ferrofluids can still be largely determined by thermal motion of the (individual) particles below the macroscopic freezing point of the system.

Experimental Section

Iron dispersions prepared by Butter et al.[11−13] were transferred to cyclohexane to perform the measurements presented here. The dispersions B−E have the radii listed in Table 1. The original iron ferrofluids were prepared by thermal decomposition of iron carbonyl in a solution of modified polyisobutene[14] (2400 g mol^{-1}) in Decalin. The full characterization, including transmission electron microscopy (TEM) and small-angle X-ray scattering, has been described elsewhere.[11−13] The data indicated the presence of an organic surface layer with a thickness of 6−7 nm. Mössbauer spectroscopy revealed that the nanoparticles consist of an iron−carbon core with the stoichiometry of $Fe_{0.75}C_{0.25}$.[15] The saturation magnetization is 1.49×10^6 A m^{-1}, somewhat less than that for pure iron (1.71×10^6 A m^{-1}).

For the measurements, the magnetic particles were transferred to cyclohexane, an organic solvent with a relatively high melting point (279.5 K).[16] In a typical procedure, 2−3 mL of the original system in Decalin was introduced in a round-bottom flask in a

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Table 1. Iron Core Radii[11] and Concentrations of the Ferrofluids

| ferrofluid | iron core radius (nm) | | concentration (mass fraction Fe) |
	a_{TEM}	a_{SAXS}	
B	6.0 ± 0.7	4.9	0.036
C	6.6 ± 1.1	6.0	0.048
D	6.9 ± 1.0	8.8	0.019
E	8.2 ± 1.5	9.5	0.016

dry nitrogen atmosphere. The solvent was removed by gently heating ($\simeq$75 °C) the system at reduced pressure. The obtained dry solid was redispersed in cyclohexane and stored under nitrogen in a closed glass tube. The concentration was determined by comparing the magnetic susceptibility to that of the original dispersion in Decalin.[11] Dynamic susceptibility spectra in cyclohexane at room temperature were comparable to the spectra in Decalin.[10]

Dynamic susceptibility measurements were performed on a home-built setup[10] with mutually inducing coils (Helmholtz configuration) placed in a cooling compartment. The spectra were recorded from 15 to 10^5 Hz in a temperature range from 263 to 293 K. The interaction energy of the alternating magnetic field (30 A m^{-1} amplitude) with the iron particles was on the order of $10^{-2}k_BT$. On this basis, it is assumed that the forces acting on the particles and aggregates were negligible and did not alter the systems. Preceding the measurements at temperatures below the freezing point of cyclohexane, the samples were instantaneously frozen (in zero applied field) by plunging them in cooled ethylene glycol (253 K) and slowly heated to the desired temperature. The applied freezing method resulted in homogeneously distributed segments of frozen dispersion due to the sudden density drop of the solvent.[16] The temperature at which the measurements were done was regulated via the cooling compartment, placed under a dry nitrogen flow. Prior to the measurements, the temperature was allowed to stabilize several hours to obtain the intended temperature in the sample. To establish the freezing point of the ferrofluids, differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC-821e with a heat rate of 2 K/min.

Results

Dynamic susceptibility spectra of ferrofluids B−E are presented in Figure 1. The corresponding spectra obtained at 263 K are indicated by B_f−E_f. Spectra recorded at 293 K before and after freezing were identical, demonstrating a reversible phase transition.

The frequency dependence of the magnetic susceptibility gives information on how fast the magnetic dipole moments in a ferrofluid reach a new steady-state average orientation by thermal motion when an alternating but weak magnetic field is applied.[9] It consists of a real χ' (in-phase) and an imaginary χ'' (out-of-phase) part.

The estimated characteristic frequencies of the studied ferrofluids at different temperatures are shown in Figure 2. The characteristic frequencies were determined by establishing the maxima of the imaginary parts of the magnetic susceptibility.

DSC measurements on the iron dispersions show a melting trajectory between 268 and 279 K (Figure 3). At 268 K and below the dispersions are macroscopically frozen (the sample can be held upside down without liquid flow). By comparison, pure cylohexane is characterized by a clear melting temperature of 279.5 K (onset).

Discussion

Ferrofluids B−E correspond to different situations and are discussed separately. In B, Néel relaxation dominates, and in C, it is the motion of single particles. D contains short dipolar chains, and E contains longer ones.

Ferrofluid B. Figure 1 shows dynamic susceptibility spectra of ferrofluid B above (293 K) and below the freezing
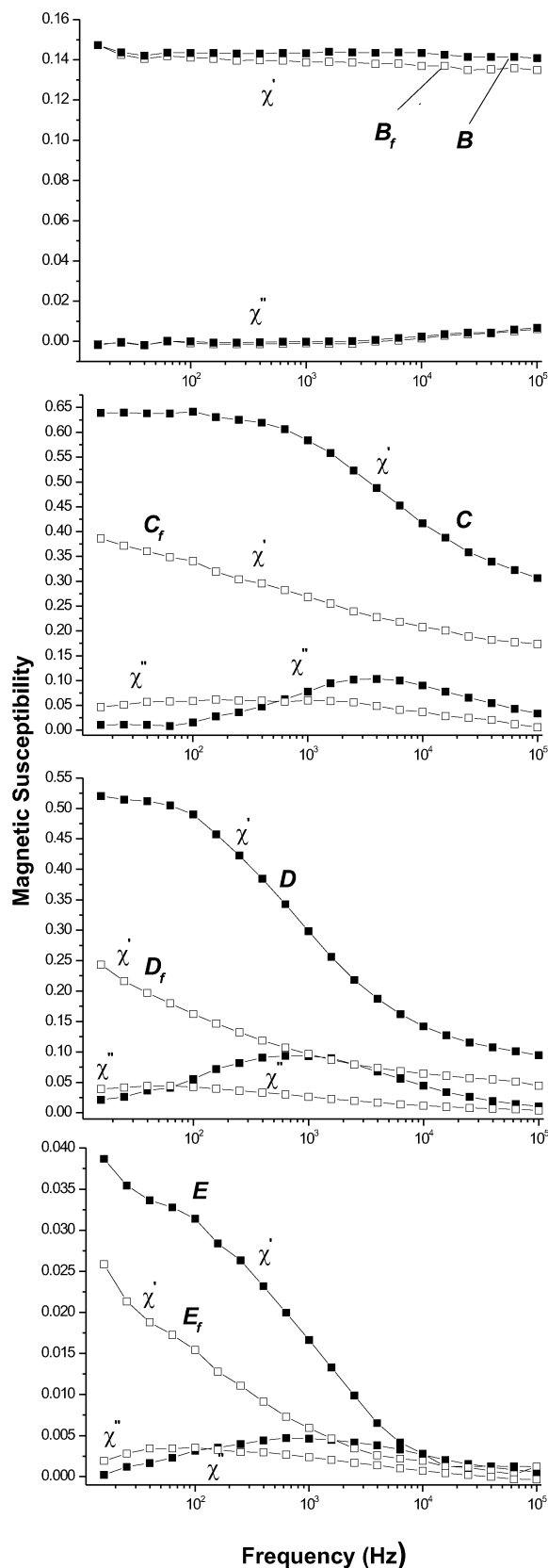

Figure 1. Frequency dependence of the real (χ') and imaginary (χ'') components of the magnetic susceptibility of ferrofluids B−E at 293 K and below the freezing point of cyclohexane at 263 K (B_f−E_f).

point (B_f) of the mixture (263 K). The signal is ascribed to rotation of the magnetic dipole moments inside the particles (Néel rotation).[10] This can be understood by comparing the theoretically predicted characteristic fre-
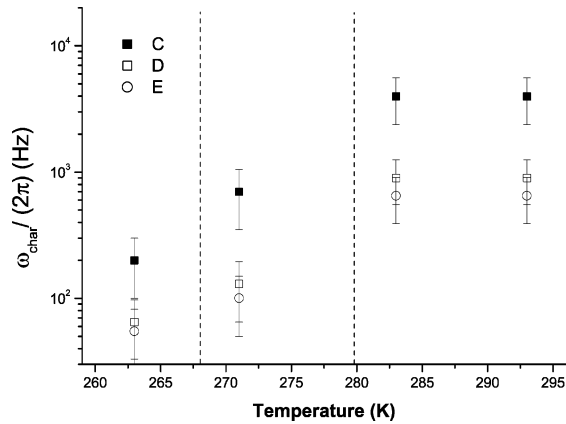
Figure 2. Estimated value of the characteristic frequency (ω_{char}) of samples C–E recorded at different temperatures. The region between the dashed lines indicates the observed melting regime. Below 268 K the sample is macroscopically frozen. The error bars correspond to a 35% error (above 280 K) and a 50% error (below 280 K) in the estimated frequency values.
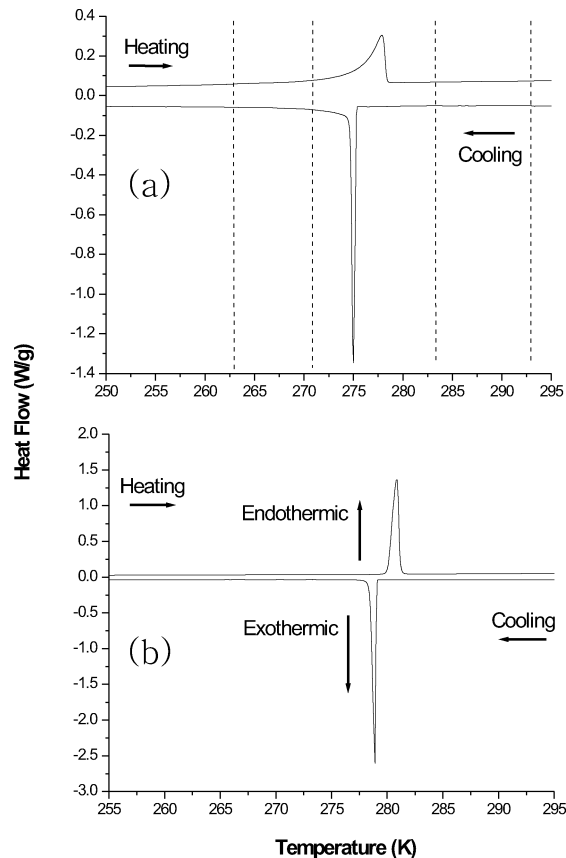

Figure 3. DSC data (a) for an iron dispersion and (b) for cyclohexane. The vertical dashed lines in part a indicate the temperatures at which the dynamic susceptibility measurements were done.

quencies for Néel and Brownian rotation of single uncorrelated particles. The characteristic frequency for Néel rotation is given by

$$\omega_{N} = 2\pi f_0 \exp\left(\frac{-KV}{k_{B}T}\right) \qquad (1)$$

where f_0 is a constant in the range 10^7–10^{12} Hz,[9,17] K is

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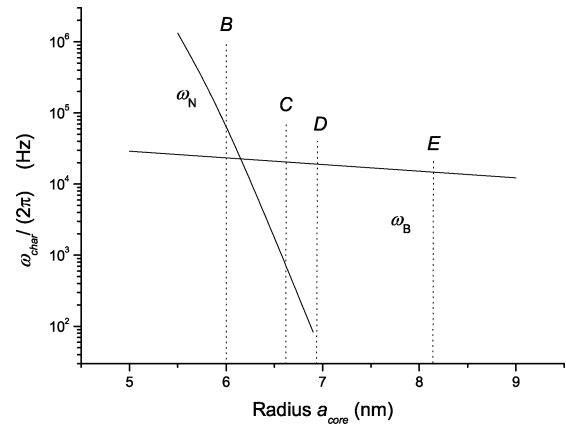
Figure 4. Calculation (eqs 1 and 2) of the Néel rotation frequency (ω_{N}) and the Brownian rotation frequency (ω_{B}) of single particles as a function of the iron core radius a_{core} (eq 2, $\eta = 1.0 \times 10^{-3}$ kg m^{-1} s^{-1}). The particles are assumed to be spherical, with $a_{h} = a_{core} + 7.0$ nm and $a_{core} = a_{m} + 1.5$ nm, where a_{m} is the magnetic radius. The calculation of ω_{N} is based on $f_0 = 10^9$ Hz and $K = 100$ kJ m^{-3}, chosen to reproduce the observed dominance of the Néel or the Brownian mechanism for ferrofluids B–E. The experimental iron core radii from TEM are indicated (Table 1).

a shape-dependent material constant, $k_{B}T$ is the thermal energy, and V is the magnetic domain volume. The characteristic frequency for Brownian rotation is given by

$$\omega_{B} = \frac{k_{B}T}{4\pi\eta a_{h}^{3}} \qquad (2)$$

where η is the viscosity of the solvent and a_{h} is the hydrodynamic radius. Figure 4 illustrates the equations by a theoretical calculation of the Néel rotation frequency and the Brownian rotation frequency of single particles as a function of the iron core radius. If the relaxation processes take place on different time scales, the measured characteristic frequency will be determined by the fastest rotation mechanism.[9] The magnetic relaxation observed for the B system is too rapid to occur for Brownian rotation.

Although measurements on the nonfrozen dispersion already unambiguously show domination of the Néel mechanism, this is confirmed by the data on the frozen dispersion. On the basis of eq 1 and considering a polydisperse system, only slight changes are expected in the characteristic frequency for Néel relaxation on going from 293 to 263 K (data between 293 and 263 K are not shown). This is supported by the results presented in Figure 1. Furthermore, it is in agreement with results obtained by Fannin et al.[6] on polydisperse colloidal magnetite dispersions.

At low frequencies the magnetic susceptibility matches the initial slope of the magnetization curve, which is directly related to the temperature

$$\chi_i = \frac{\mu_0 \mu M_s}{3 k_{B} T} \qquad (3)$$

where μ_0 is the permeability of vacuum, μ is the magnetic dipole moment, and M_s is the saturation magnetization per unit volume. According to eq 3, χ_i increases with decreasing temperature, but within the applied temperature range this is hardly observed.

Ferrofluid C. For ferrofluid C, the majority of the magnetic particles have a characteristic frequency of about 4 kHz. As discussed in Erné et al.[10] and according to Figure

4, it can be deduced that this frequency is of the order expected for the Brownian rotational diffusion of single uncorrelated particles. Because of polydispersity, a significant number of smaller magnetic particles are also present, whose magnetic moments relax by the Néel mechanism.

Comparing the measurements of the frozen (C_f) and the liquid (C) state reveals a major displacement of the relaxation frequencies to lower values. On the basis of the maximum of the imaginary part, the estimated characteristic frequency of the magnetic particles in the frozen state is about 200 Hz at 263 K. This considerable decrease of the characteristic frequency points out that, for most particles in ferrofluid C, the magnetic moment is blocked within the particle. As a result, the alignment of the dipoles in the applied alternating magnetic field can only happen by rotation of the particles themselves. One might expect that freezing the dispersion would cause mechanical rotation to stop.
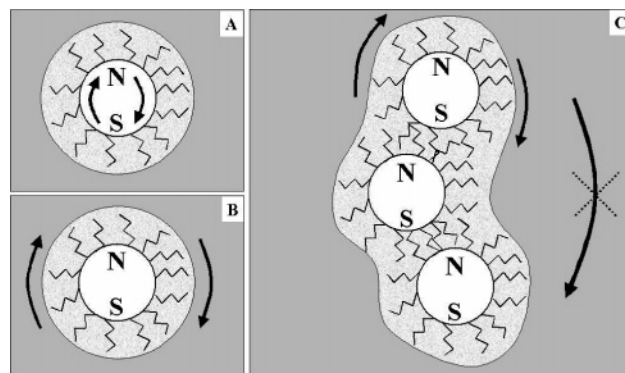
However, the measurements clearly indicate that motion of the particles still occurs in the macroscopically frozen state. The likely explanation is that the magnetic cores of the particles are able to move because their local environment is not frozen cyclohexane but nonfrozen polymer. This is the polyisobutene coating on the magnetic cores responsible for steric stabilization. The organic layer at the surface of the particles can be seen as a highly concentrated polymer solution, whose melting point is significantly lower than that of the pure solvent. Pure polyisobutene has a glass transition at about 200 K[18] and is highly viscous ($\eta > 1.0$ Pa·s for our polymers at room temperature).[14] The motion of the magnetic particles below the macroscopic freezing point would be less pronounced in the case of a thinner surfactant layer (here about 7-nm thick).

The low-frequency limit, now below our frequency range at 263 K, is not expected to change much within the applied temperature range. However, this assumes that the dipoles do not lose the possibility to reorientate themselves, be it by Néel rotation at very low frequencies.

Upon going from 293 to 285 K, the viscosity of the solvent increases by 30%.[19] This means that, on a logarithmic scale, the characteristic frequency only shifts 0.1 to lower values (eq 2). As a result, between 293 K and the initial freezing point, no noticeable changes in the spectrum are detected.

Ferrofluid D. At room temperature a broad distribution of ω_{char} around 900 Hz can be observed for ferrofluid D. Because the frequency for the Brownian rotation of single particles is calculated around 11 kHz (eq 2), the frequency distribution at 900 Hz indicates the presence of aggregates in the dispersion. According to a previously described relation,[10] this frequency range should correspond to aggregates of two to three particles. The size of the aggregates, however, depends on the concentration of the magnetic particles in the dispersion.[10]

Freezing the sample results in a drastic decline of ω_{char} to frequencies well below 100 Hz. As with ferrofluid C_f, the magnetic susceptibility does not decrease to 0 upon freezing. Instead, it appears that the magnetic particles or aggregates are still able to react to the applied alternating magnetic field. Dipolar chains are still present, because otherwise a characteristic frequency would be

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Figure 5. (A) Néel relaxation is not affected by freezing the ferrofluid. (B) Rotation of single particles in a frozen solvent may still occur as a result of the low melting point of the organic surface layer. (C) End-over-end rotation of the chain as a whole is highly unfavorable in a frozen ferrofluid. However, local wiggling of the individual particles in the chain may still occur.

expected comparable to that found for ferrofluid C_f (ω_{char} is a weak function of the iron core radius, see Figure 4.)

However, freezing the solvent was expected to have a stronger effect in the presence of dipolar chains. Because thermal motion of single particles is inhibited in a frozen solvent (ferrofluid C), end-over-end rotation of an entire dipolar chain is likely to be slowed more drastically or even stopped completely (explained in Figure 5). Nevertheless, the frequency decline of ferrofluid D with dipolar chains seems to be comparable to the frequency decline of ferrofluid C without dipolar chains (see Figure 2).

In the smaller particles (system B), which exhibit Néel relaxation (see Figure 5A), the viscosity of a solvent has no impact on dipole rotation in the particle. The rotation of single particles in a frozen solvent (system C) can be considered as the motion of a sphere in a spherical cavity filled with polymers (see Figure 5B). Figure 5C reflects the situation concerning dipolar chains in a macroscopically frozen solvent. End-over-end rotation of a chain appears practically excluded. Nevertheless, although the particles are correlated, local thermal wiggling of single particles in a chain may still be possible. In other words, local motion of the individual particles in a chain becomes the dominating mode of thermal motion. In this case, the dipole−dipole interactions are expected to lead to somewhat lower values of ω_{char} in comparison with single uncorrelated particles (as in system C).

Ferrofluid E. In ferrofluid E, at room temperature, a major part of the particles are in aggregates rotating with a characteristic frequency of approximately 650 Hz. This value indicates relatively large aggregates composed of more than two to three particles.[10] In the frozen state (263 K) a characteristic frequency is found below 100 Hz. This is somewhat lower than that detected for ferrofluid C_f. Furthermore, the data presented in Figure 2 give the impression that freezing has a comparable impact on the E and D systems.

The observation that the 15-Hz susceptibility of sample E is a factor of 13 lower than that of sample D at comparable concentrations agrees with our previous findings.[10] It likely has to do with the fact that the low-frequency limit is not reached in the spectra of sample E and, therefore, the quantitative link between concentration and susceptibility is difficult to establish. Furthermore, cryo-TEM pictures of sample E show the presence of large semispherical clusters of dipolar chains (aggregates),[12] of which the net contribution to the suscep-

tibility is unclear. In contrast, cryo-TEM pictures of sample D do not show these clusters but demonstrate more linear structures.

The fact that the low-frequency limit is not reached in the spectra of the frozen samples and the samples containing aggregates is a limitation of the measurements. Nevertheless, the spectra allow a much more detailed interpretation than if measurements had only been performed at a single (low) frequency.

Conclusion

Dynamic susceptibility measurements provide direct information about the degree of dipole−dipole interactions between magnetic nanoparticles in a ferrofluid. Here, for instance, the technique establishes the presence of dipolar chains in iron dispersions D and E. Measurements on frozen dispersions can be performed to determine unambiguously whether Brownian rotation or Néel rotation dominates the relaxation mechanism in single particles or aggregates. Although in principle Néel relaxation is expected to be the only relaxation mechanism, our measurements on macroscopically frozen iron dispersions show that the local viscosity near the colloids, in contrast to the frozen macroscopic bulk, may still be finite. As a result, local motion of the particles or the chain itself still occurs. Thermal motion of single particles is substantially slowed in a macroscopically frozen solvent. Therefore, it was expected that the motion of dipolar chains would be slowed much more and that end-over-end rotation should even stop completely. Because considerable thermal motion can still be detected, this suggests that the motion corresponds to local thermal wiggling of individual particles in a chain.