

HYSTERESIS EFFECT IN A COLLOIDAL SUSPENSION OF MAGNETIC BEADS¹

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Abstract

Results of the measurement of the frequency and field dependence of the complex magnetic susceptibility, $\chi_s(\omega) = \chi'_s(\omega) - i\chi''_s(\omega)$, of a water based colloidal suspension of 200nm magnetic beads containing single domain maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles, are presented.

Measurements are performed over the frequency range 200 Hz to 1 MHz whilst the polarizing field, H , is varied over the range 0-13.6 kA/m, initially in a forward direction, and then in a reverse direction and from a plot of the static susceptibility, χ_{0s} , against H , the existence of a hysteresis effect is confirmed.

Under the increasing polarizing field an absorption peak is detected in the imaginary susceptibility component at frequencies f_{max} between 1.26 and 2.15 kHz. It is confirmed that the absorption peak can be attributed to the Néel relaxation of the inner maghemite nanoparticles.

Keywords: Ferrofluid; Magnetic fluids, Magnetic beads, Relaxation;

PACS: 75.50.Mm Magnetic fluids; 76.60.Es Relaxation effects;

1. Introduction

Superparamagnetic colloids [1] are presently used in many fundamental areas of research. For instance, the use of such colloids with beads coated with antibodies that specifically bind to specific proteins is of current interest in the area of medical diagnosis [2].

The magnetic spheres investigated here have a diameter of 200 nm [3] and were made by evaporating the solvent (octane) in emulsions of an organic ferrofluid. These solid-like spheres contain 50% volume fraction of maghemite particles of approximately 10 nm mean radius (as measured by Dynamic Light Scattering), the surfactant being oleic acid. With spheres of this diameter the dominant relaxation mechanism could be due to either Brownian [4] or Néel relaxation [5]. However, the inner maghemite particles are extremely confined inside the spheres (almost close-packed) and therefore cannot experience Brownian relaxation. The only possible contribution of the inner, single domain, particles is thus their Néel relaxation, as has been previously confirmed [6].

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Single domain particles have a magnetic moment, m_p , given by, $m_p = M_s v$ where M_s denotes the saturation magnetisation and v is the magnetic volume of the particle.

The Brownian relaxation time τ_B is given by [4]: $\tau_B = 4\pi r^3 \eta / kT$ (2)

where r is the hydrodynamic radius of the particle, η is the dynamic viscosity of the carrier liquid, k is Boltzmann's constant and T is the absolute temperature.

In the case of the Néel relaxation mechanism, the magnetic moment may reverse direction within the particle by overcoming an energy barrier, which for uniaxial anisotropy, is given by Kv , where K is the anisotropy constant of the particle. The associated reversal or switching time τ_N was estimated by Néel to be:

$$\tau_N = \tau_0 \exp(\sigma) \quad (3)$$

τ_0 being a damping time having an approximate value of 10^{-9} s and $\sigma = Kv/kT$.

When a sample contains a distribution of particle sizes, both relaxation mechanisms contribute to the magnetisation. They do so with an effective relaxation time τ_{eff} [7, 8], where

$$\tau_{eff} = \tau_N \tau_B / (\tau_N + \tau_B), \quad (4)$$

the mechanism with the shortest relaxation time being dominant.

2. Complex susceptibility

The frequency dependent susceptibility, $\chi(\omega)$, may be written in terms of its real and imaginary components, where,

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega). \quad (5)$$

The theory developed by Debye [9] to account for the anomalous dielectric dispersion in dipolar fluids has been used [10-12] to account for the analogous case of magnetic fluids in the approximate range 10 Hz to 1 MHz.

According to Debye's theory the complex susceptibility, $\chi(\omega)$, has a frequency dependence as given by the approximate equation,

$$\chi(\omega) = \chi_0 / (1 + i\omega\tau_{eff}) = \chi_0 (1 / (1 + \omega^2\tau_{eff}^2) - i\omega\tau_{eff} / (1 + \omega^2\tau_{eff}^2)). \quad (6)$$

where the static susceptibility, χ_0 , is given by,

$$\chi_0 = nm^2 / 3kT\mu_0 \quad (7)$$

and

$$\tau_{\text{eff}} = 1 / \omega_{\text{max}} = 1/2\pi f_{\text{max}}, \quad (8)$$

where f_{max} is the frequency at which $\chi''(\omega)$ is a maximum, and n is the particle number density.

Thus by determining f_{max} equation (8) enables one to obtain the mean particle or aggregate size of the sample.

As the measurement frequency increases beyond approximately 1 MHz, a transition from relaxation to resonance occurs. $\chi(\omega)$, of an assembly of single domain particles can also be described in terms of its parallel, $\chi_{\parallel}(\omega)$, and perpendicular, $\chi_{\perp}(\omega)$, components, with [13]

$$\chi(\omega) = \frac{1}{3} (\chi_{\parallel}(\omega) + 2\chi_{\perp}(\omega)) \quad (9)$$

$\chi_{\perp}(\omega)$ can have a resonant character, whereby precession of the magnetic moment occurs about an easy axis (i.e. the direction of the internal field H_A).

Under equilibrium conditions, the magnetic moment, m_p , and the anisotropy field, H_A , of a particle are parallel and any deviation of the magnetic moment from the easy axis direction results in the precession of the magnetic moment about this axis. If the polar angle is small, the angular resonant frequency, ω_{res} , is given by [14],

$$\omega_{\text{res}} = \gamma H_A \quad (10)$$

H_A is the internal field for a particle with uniaxial anisotropy and where the polar angle between the easy axis and the magnetic moment is small, has magnitude, $H_A = 2K / M_s$, where K is the anisotropy constant in J/m^3 .

From equation (10) it can be seen that the effect of applying an external polarising field, H , results in an increase in the resonant frequency ω_{res} , which can be described approximately by

$$\omega_{\text{res}} = 2\pi f_{\text{res}} = \gamma(H + \bar{H}_A), \quad (11)$$

where \bar{H}_A represents some mean value of the anisotropy field. Equation (11) is the equation of a straight line and from a plot of f_{res} against H , the value of \bar{H}_A can be determined from the intercept of the plot with the x-axis.

3. Experimental and Results

Measurements were firstly performed on the base ferrofluid, Sample 1, which was a suspension of maghemite ($\gamma\text{Fe}_2\text{O}_3$) particles of mean particle radius 10 nm in octane, with oleic acid as surfactant. This was realized by means of low frequency, 100 Hz to 0.1 MHz and high frequency, 100 MHz to 6 GHz, complex magnetic susceptibility measurements.

Low-frequency measurements were made to determine whether or not the sample was aggregated and this was accomplished by means of the toroidal technique [15] in conjunction with a Hewlett Packard RF Bridge 4291A. The sample was found to be un-aggregated [6].

The higher frequency range measurements were made by the short-circuit transmission line technique [16, 17]. The measurements were performed at different values of polarising field over the range 0 to 110 kA/m in order to determine \bar{H}_A and subsequently \bar{K} ; the latter value being need to calculate τ_N in equation (3).

Fig 1. shows a normalized plot $\chi'(\omega)$ and $\chi''(\omega)$, against frequency of the components of complex magnetic susceptibility, at zero polarizing field. For the unpolarised case $f_{\max} = 1.15$ GHz and $f_{\text{res}} = 1.8$ GHz and over the polarizing field range f_{\max} and f_{res} were found to increase to 5.0 and 5.2 GHz respectively.

From equation (11), the field dependence of f_{res} is given by $2\pi f_{\text{res}} = \gamma(H + \bar{H}_A)$ and from a plot of f_{res} against H , \bar{H}_A , of the maghemite particles of Sample 1 was determined as being 47.8 kA/m as can be seen from Fig 2. Using an M_s of 0.4 T, the anisotropy constant, \bar{K} , is determined as $\bar{K} = M_s H_A / 2 \approx 10^4 \text{ J/m}^3$.

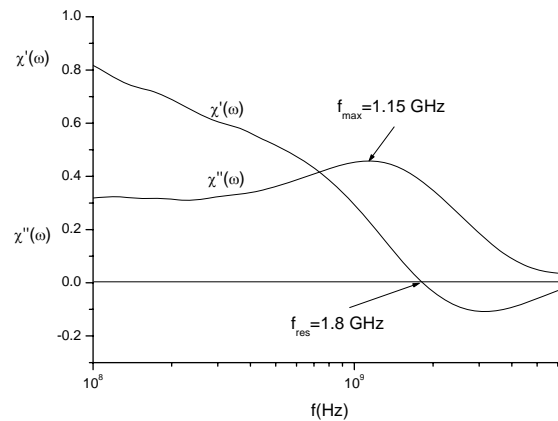


Fig 1. Plot of $\chi'(\omega)$ and $\chi''(\omega)$ against $f(\text{Hz})$ over the range 10^8 to $6 \cdot 10^9$ Hz, for Sample 1.

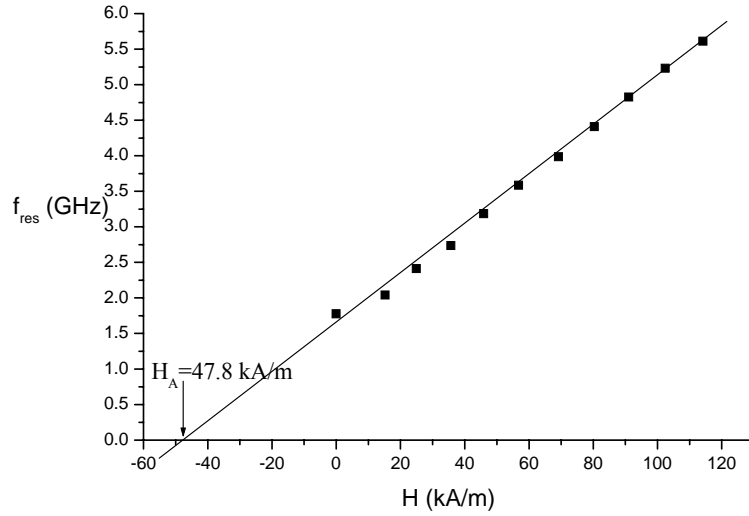


Fig 2. Plot of f_{res} against polarizing field ,H, for Sample 1.

Complex susceptibility measurements, $\chi_s(\omega) = \chi'_s(\omega) - i\chi''_s(\omega)$, were then performed on the suspension of magnetic spheres, Sample 2. Fig 3. shows a plot of the static susceptibility χ_{0s} against H obtained for both forward and reverse directions of polarisation, (χ_{0s} was taken to be equivalent to the values of $\chi'_s(\omega)$ obtained at 400Hz). In the case of increasing values of H, this figure shows an overall trend of increasing values of χ_{0s} , up to a value of approximately 0.11; this is in contrast to what happens in the case of magnetic fluids[18] where the equivalent components decrease with increasing H.

Fig 3 also shows that with decreasing H, χ_{0s} , initially increases. This latter increase continues until, at an approximate value of H =5,000 A/m, there is a slight leveling off followed by a decrease to a value of 0.11 for H=0. This is thus a manifestation of a hysteresis effect which was the object of this work and unlike that reported in [6], in this case the presence of a large remenence at H=0, is indicated.

Fig 4. shows the corresponding variation in the absorption peak, f_{max} , with the cyclic variation in H. The absorption peak is first detected at a frequency of $f_{max} = 1.26$ kHz, for H= 0.9 kA/m, and increases to $f_{max} = 2.15$ kHz for H= 13.6 kA/m. Then, with a reversal of H, f_{max} decreases, in the manner shown in Fig 4.

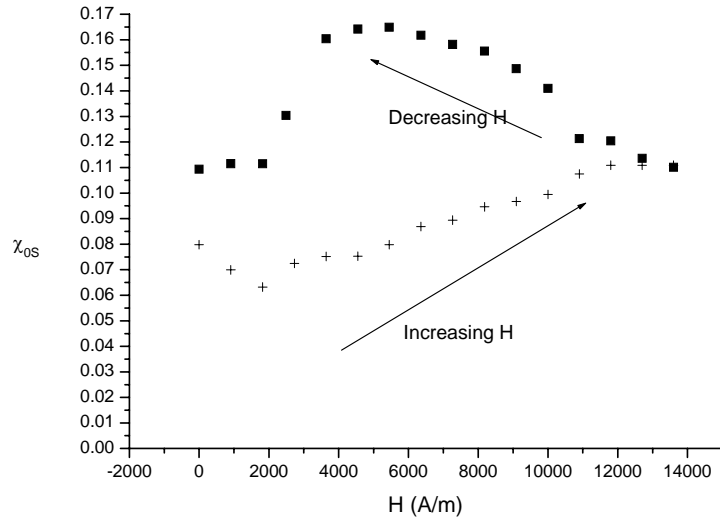


Fig 3. Plot of χ_{0s} against H, in a forward and reverse direction , for Sample 2.

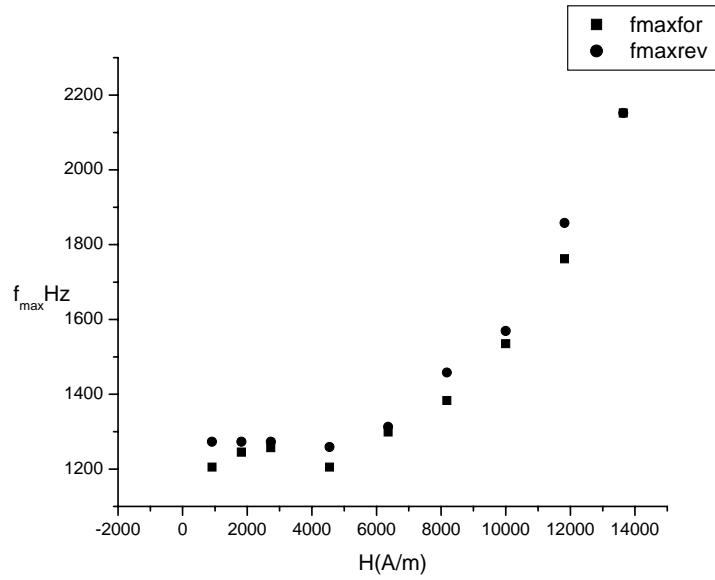


Fig 4. Plot of f_{max} against H, in a forward and reverse direction, for Sample 2.

4. Discussion

The first issue requiring discussion is why the complex components, $\chi'_s(\omega)$ and $\chi''_s(\omega)$, increase with increasing polarising field.

From (6), it can be seen that both $\chi'_s(\omega)$ and $\chi''_s(\omega)$, are directly proportional to χ_{0s} , and since $\chi_{0s} = nm_{ps}^2/3kT\mu_O$, all parameters are fixed except for m_{ps} , the effective magnetic moment of the spheres. Thus an increase in m_{ps} could be due to the fact that the individual

spheres and magnetic moments in the spheres are becoming more aligned with increasing H. So from (6) both $\chi'_s(\omega)$ and $\chi''_s(\omega)$ should increase with increasing H, as they indeed do. Also, a factor which influences the variation in $\chi'_s(\omega)$ and $\chi''_s(\omega)$ with H, is the customary diminution of $\chi(\omega)$ due to the Langevin profile of the magnetization and this may be a contributing factor, for example, in the flattening of the χ_{0s} against H profile at higher fields. Fig 3. also shows how χ_{0s} initially increases with decreasing H until an approximate value of $H=5,000$ A/m is reached; it then decreases rapidly with further decrease in H, to a value of $\chi_{0s} = 0.11$ at $H=0$. This level of remanence corresponds to the equilibrium level attained in the fluid when H was increased up to 13.6 kA/m on the forward cycle of polarisation.

At this point in time we are unable to fully explain this behaviour and it is currently under further investigation. However we note that the spherical droplets are assumed to remain spherical under the influence of the polarizing field. If this were not so it would have consequences from the de-mag factor of the droplets and hence the magnitude of the static susceptibility, χ_{0s} .

The second issue to be considered is that of the determination of the relevant relaxation mechanism of the suspension of magnetic beads. To do this we shall estimate the order of magnitude of the three possible relaxation frequencies.

Experimentally, we have:

$$\tau_{\text{eff}} = 1/\omega_{\text{max}} = 1/2\pi f_{\text{max}}$$

In the case of Brownian relaxation (from (2)) there comes

$$1/2\pi f_{\text{max}} = 4\pi\eta r^3 / kT, \text{ giving, } f_{\text{max}} = kT/8\pi^2 r^3 \eta$$

So if we assume negligible change in viscosity, η , the increase in f_{max} over the polarising field range, corresponds to a decrease in the effective hydrodynamic radius, r , of the spheres.

In the case of the magnetic spheres in a water based carrier, using a radius of 100 nm, at room temperature the Brownian relaxation time is given by:

$$\tau_B = 4\pi\eta r^3 / kT = 4\pi \cdot 10^{-27} \cdot 10^6 \cdot 10^{-3} / 4 \cdot 10^{-21} \approx 3 \cdot 10^{-3} \text{ s}$$

resulting in $f_{\text{max}} = 1/6\pi \cdot 10^{-3} \approx 50$ Hz. This frequency is well outside the frequency range where the loss-peaks are detected.

In the case of Néel relaxation, (from (3))

$$\tau_N = \tau_0 \exp(\sigma) \text{ with } \tau_0 \approx 10^{-9} \text{ s}$$

Thus for spheres of 100nm radius, with $K \approx 10^4 \text{ J/m}^3$ (as determined from our high frequency measurements), we get a value of $\sigma \approx 1 \cdot 10^4$ which corresponds to an almost infinite relaxation time that is to say to an undetectable (almost zero) frequency.

However, for a 10 nm particle, with $K \approx 10^4 \text{ J/m}^3$, we get a value of $\sigma = 10.5$ and $\tau_N = 3.6 \cdot 10^{-5} \text{ s}$. The corresponding $f_{\max} = 1/(2 \pi \tau_N) \approx 4 \text{ kHz}$, which is in line with the measured loss-peaks (between 1 and 2 kHz). Thus from the above calculations of the Néel and Brownian relaxation times it appears that the loss-peaks detected have their origins in the Néel relaxation of the inner maghemite particles. This confirms previous published data [], where, to conclusively confirm that Néel was the dominant relaxation mechanism, the susceptibility measurements were repeated with the viscosity of the carrier being increased 1000 times (by changing the carrier from water to glycerine). The result of this exercise showed that the frequency, f_{\max} , of the loss peaks were unchanged. Since, from equation (2), τ_B is directly proportional to the viscosity, η , and from equation (3) τ_N is independent of η , this result thus confirms that Néel relaxation of the inner particles is responsible for the loss-peaks.

5. Conclusion

In this work, measurements of the frequency dependent, complex susceptibility, $\chi_s(\omega) = \chi'_s(\omega) - i\chi''_s(\omega)$, over the frequency range 200 Hz to 1 MHz, of a magnetic colloid consisting of spherical beads of 200 nm diameter, containing maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles, have been presented. From a plot of the static susceptibility, χ_{0s} , against polarizing field, H , in a forward and then a reverse direction, a hysteresis effect together is demonstrated. The relaxation properties of the colloid are also investigated and it is confirmed that the absorption peak of the $\chi''_s(\omega)$ component, over the measured frequency range, is due to Néel relaxation of the inner maghemite particles.

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References

- [1] Montagne, F, Mondain-Monval, O, Pichot, C, H.Mozzanega, H and Elaissari, A, J. Magn. Mater, 250 (2002) 302.
- [2] Baudry, J., Bertrand, E., Lequeux, N. and Bibette J., J. Phys. Cond. Matt. 16 (2004) 469.
- [3] www.ademech.com
- [4] Brown, W.F., J. Appl. Phys.34 (1963) 1319.
- [5] Néel, L., Ann. Géophys. 5 (1949) 99.
- [6] Fannin, P.C., Cohen-Tannoudji, L., Bertrand, E.,Giannitsis, A.T., Mac Oireachtaigh,C., Bibette, J. In Press, J.Magn.Magn.Mater.
- [7] M.I.Shliomis, Sov. Phys.-Usp. 17 (1974) 53.
- [8] Shliomis, M.I., and Raikher, Yu.L, IEEE Trans .Magn., Mag-16,(1980) 237
- [9] Debye. P, Polar Molecules (The Chemical Catalog Company, New York, 1929).
- [10] Maiorov, M.M., Magnetohydrodynamics (cover-to-cover translation of Magnitnaia Hidrodinamika) 2 (1979) 21, 135.
- [11] Fannin, P.C., Scaife, B.K.P., and Charles, S.W., J. Magn. Mater, 72 (1988) 95.
- [12] Fannin, P.C., J.Mol.Liq., 69 (1996) 39.
- [13] Raikher ,Y.L., and Shliomis, M.I.,Sov. Phys. JETP 40, (1975) 526.
- [14] Shliomis, M.I., and Raikher, Yu.L,IEEE Trans.Magn., Mag-16,(1980) 237.
- [15] Fannin, P.C., Scaife, B.K.P., and Charles, S.W., J. Phys. E. Sci. Instrum., 19 (1986) 238.
- [16] S.Roberts, S, and von Hippel, A.R, J.App.Phys., 17 (1946) 610.
- [17] Fannin, P.C., Relihan, T. and Charles, S.W., J. Phys. D:Appl. Phys. 28, (1995) 10, (2003).
- [18] Fannin, P.C., and Giannitsis, A.T, J.Mol.Liq., 114 (2004) 8.