Analele Universităţii de Vest din Timişoara
Vol. XLVIII, 2006
Seria Fizică

INVESTIGATING THE PROPERTIES OF MAGNETIC FLUIDS BY MEANS OF POLARISED MEASUREMENTS

P.C.Fannin

Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Ireland.
email:pfannin@tcd.ie

Abstract
Field and frequency-dependent, complex susceptibility, $\chi(\omega, H)=\chi'(\omega, H)-i\chi''(H, \omega)$, measurements is a well established method for investigating the dynamic properties of magnetic fluids. Polarised measurements have been used to investigate many properties, including, relaxation mechanisms, the presence or absence of aggregates, and associated magnetic losses. Also, important information on the effect which polarised measurements have on on the hysteresis and isotropic properties of samples can also be obtained through the use of polarised measurements.In this paper examples of the determination of the above mentioned properties on two magnetic fluid samples, by means of the toroidal technique over the frequency range *200 Hz* to *1 MHz*, are presented and discussed.

Key words: Magnetic fluids; Complex susceptibility; Relaxation effects

1. Introduction

Magnetic fluids consist of colloidal suspensions of nanoparticles of ferromagnetic or ferrimagnetic materials dispersed in a carrier liquid and stabilised by a suitable organic surfactant. The surfactant coating creates an entropic repulsion between particles [1], such that thermal agitation alone is sufficient to maintain them in a stable dispersion. The particles are single-domain and are considered to be in a state of uniform magnetisation with magnetic dipole moment (Wb m),

$$m=M_s\, v \tag{1}$$

where M_s is the saturation magnetisation (Wb/m^2) of the of the material and v is the magnetic volume of the particle. The preferred orientation of the magnetic moment is along an axis, or axes, of easy magnetisation and this direction depends generally on a combination of shape and magneto-crystalline anisotropy denoted by the symbol K. Also, when in suspension their magnetic properties can be described by the Langevin function ($L(\xi)$), suitably modified to take

account of a distribution of particle sizes. The magnetisation M is described by the Langevin expression,

$$M = M_s\,[coth\xi - 1/\xi] \tag{2}$$

$\xi = mH/kT$, where k is Boltzmanns constant and H the magnetizing field.

One convenient method of investigating the dynamic properties of magnetic fluids is by measurement of the frequency-dependent complex, relative susceptibility, $\chi(\omega)$, which may be written in terms of its real and imaginary components, where

$$\chi'(\omega) = \chi'(\omega) - i\chi''(\omega) \tag{3}$$

It has been shown that the theory of Debye [2] developed to account for the anomalous dielectric dispersion in dipolar fluids may be used [3, 4, 5] to account for the analogous case of magnetic fluids. According to Debye's theory, $\chi(\omega)$ has a frequency dependence given by the equation,

$$\chi(\omega) = \frac{\chi_0 - \chi_\infty}{1 + i\omega\tau_{eff}} + \chi_\infty \tag{4}$$

where the static susceptibility

$$\chi_0 = \frac{nm^2}{3kT\mu_0} \tag{5}$$

χ_∞ is the high frequency susceptibility at a frequency below that of resonance, m is the particle magnetic moment, n is the particle number density, τ_{eff} is the effective relaxation time and μ_0 is the permeability of free space.

A typical Debye type spectra is shown in Fig1 where the loss or $\chi''(\omega)$ component displays a peak at a frequency f_{max}. However, the Debye model assumes the ferrofluid to consist of particles of uniform size and so one would expect the shape of a samples spectra to differ from that of Fig 1. This is illustrated in Fig 2 which shows the effect of incorporating a normal distribution of radii, of standard deviation σ, into the Debye model.

The magnetic moment of the particles may relax through either rotational Brownian motion of the particle within the carrier liquid, with relaxation time τ_B [6] or through the Néel mechanism with relaxation time τ_N [7]. However over the frequency range measured here, the dominant relaxation mechanism will be considered to be τ_B .

The Brownian relaxation time τ_B is given by [6]

$$\tau_B = \frac{4\pi r^3 \eta}{kT} \tag{6}$$

where r is the hydrodynamic radius of the particle, η is the dynamic viscosity of the carrier liquid and k is Boltzmann's constant.

τ_B is related to the frequency f_{max} (Fig 1.) by the expression,

$$\tau_B = \frac{1}{2\pi f_{\max}} = \frac{4\pi r^3 \eta}{kT} \tag{7}$$

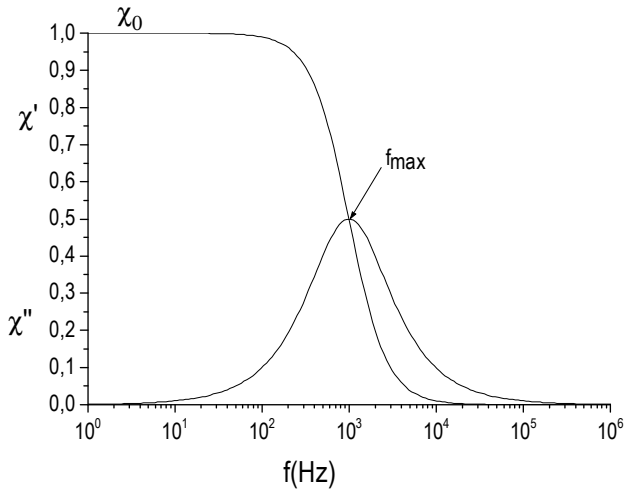

Fig 1. Debye type profile, plot of $\chi'(\omega)$ and $\chi''(\omega)$ against frequency f(Hz).

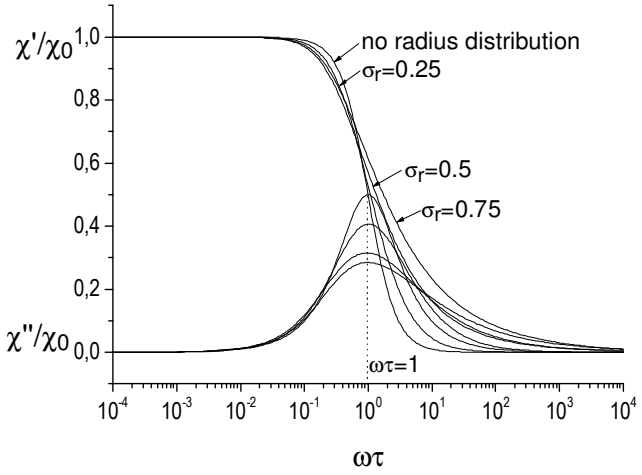

Fig 2. Debye type profiles (including a normal distribution of particle radii, of standard deviation, σ) of $\chi'(\omega)/\chi_0$ and $\chi''(\omega)/\chi_0$ against frequency f(Hz).

Thus by determining f_{max} equation (7) enables one to obtain the particle or aggregate size for the sample under investigation. The formation of aggregates [8, 9, 10,] can arise due to the effects of short range van der Waals attraction or by the effects of magnetic dipolar interactions between particles [11].

1.1 Field Dependence.

Assuming the Langevin function for the magnetization of the fluid, an expression for the field dependence of the A.C susceptibility, $\chi(\omega, H)$, can be written as follows[12],

$$\chi(\omega,\mathrm{H}) = \frac{\chi_0(1+\mathrm{f}(\mathrm{H})) - \chi_\infty}{1+\mathrm{i}\omega\tau_{\mathrm{eff}}} + \chi_\infty \tag{8}$$

with,

$$(1+\mathrm{f}(\mathrm{H})) = 3\left[1+\left(\frac{\mathrm{kT}}{\mathrm{mH}}\right)^2 - \coth^2\left(\frac{\mathrm{mH}}{\mathrm{kT}}\right)\right] \tag{9}$$

and where [13]

$$\tau_{eff} = \tau_{(H=0)}\frac{\xi - 2L(\xi) - \xi L(\xi)^2}{L(\xi)} \tag{10}$$

with $\xi = mH/kT$.

For increasing values of polarising field, equations (8) and (9) predict, respectively,

i) a reduction in both $\chi'(\omega)$ and $\chi''(\omega)$ with increasing biasing field and,

ii) a corresponding shift in f_{max} to higher frequencies.

1.2 Magnetic Losses

Magnetic losses of magnetic fluids may be expressed in terms of the loss tangent, $\tan\delta$ [14, 15, 16, 17], which is also known as the dissipation factor. This property can be investigated via the permeability of the magnetic fluid, $\mu(\omega) = \mu'(\omega) - i\mu''(\omega)$

where

$$\tan\delta = \frac{\mu''(\omega)}{\mu'(\omega)} = \frac{\chi''(\omega)}{1+\chi'(\omega)} \tag{11}$$

Furthermore, the mean heat per unit volume, T J/m^3, [17 , 18] of the sample to be easily determined from the $\chi''(\omega)$ data since, $T = \pi\chi''\mu_o h^2$ J/m^3 (12)

where *h* is the a.c. probing field.

1.3 Isotropic and Hysteresis properties

In the previous paragraphs, the usefulness of the measurement of $\chi''(\omega, H)$ has been readily demonstrated. However the question arises as to weather, upon removal of the polarising field, the ferrofluid returns to its original un-polarised state.

Thus one is interested to determine if the properties of the un-magnetised fluid remain isotropic after being subjected to a cycle of magnetization.

If the susceptibility, χ, depends upon ω and on polarising field, H, then according to the Weierstrass hypothesis [19, 20] which states that any continuous function, i.e. $\chi(\omega, H)$, on a closed and bounded interval can be uniformly approximated on that interval by polynomials to any degree of accuracy, we can express $\chi(\omega, H)$ as

$$\chi(\omega, H) = a_o(\omega) + a_1(\omega)H + a_2(\omega)H^2 + a_3(\omega)H^3 + a_4(\omega)H^4 + \ldots \quad (13)$$

and for $\omega=0$, $$\chi(0, H) = a_o(0) + a_1(0)H + a_2(0)H^2 + a_3(0)H^3 + a_4(0)H^4 \ldots. \quad (14)$$

If the fluid is isotropic, then $\chi(\omega, H) = \chi(\omega, -H)$.

Consequently, under such conditions,

$$a_o(\omega) + a_1(\omega)H + a_2(\omega)H^2 + a_3(\omega)H^3 + a_4(\omega)H^4 =$$

$$= a_o(\omega) - a_1(\omega)H + a_2(\omega)H^2 - a_3(\omega)H^3 + a_4(\omega)H^4 \ldots., \quad (15)$$

which is only possible if

$$a_1(\omega) = a_3(\omega) = a_5(\omega) = 0 \quad (16)$$

Thus we expect to be able to expand $\chi(\omega, H)$ in a series of even powers of H, i.e.

$$\chi(\omega, H) = a_0(\omega) + a_2(\omega)H^2 + a_4(\omega)H^4 \ldots\ldots + a_{2n}(\omega)H^{2n}, \quad (17)$$

which means that the graph of $\chi(\omega, H)$ vs H is symmetrical about the vertical axis.

2. Experimental and Results

Complex magnetic susceptibility measurements, over the frequency range *200 Hz* to *1 MHz,* were made by means of the toroidal technique [21] in conjunction with a Hewlett Packard RF Bridge 4291A. Here a high permeability toroid wound with twenty excitation turns was used. A second coil comprising of 3 turns was also wound on the toroid and connected to a stabilized d.c. supply to provide biasing magnetic fields, *H*. The results presented are for two ferrofluid

samples, 1) a *300G* colloidal suspension of cobalt ferrite in a hydrocarbon, isoparm, of mean particle radius *5nm*, with an oleic acid surfactant with *H* being varied over the range *0* to *13.6* kAm^{-1}, and 2) a *100G* colloidal suspension of magnetite in isoparm, of mean particle radius *5nm*, with an oleic acid surfactant, with *H* being varied from *0* up to *+13.6 kA/m* back down to *0*, down to *-13.6 kA/m* and back up to *0*.

Figs 3 and 4 show plots of $\chi'(\omega, H)$ and $\chi''(\omega, H)$ obtained for sample 1 over the polarising field range, and all are shown to have Debye type profiles with f_{max} varying from *790 Hz* to *22.4 kHz*. This observed increase in f_{max} is indicative of a decrease in effective relaxation time with a corresponding apparent decrease in average hydrodynamic aggregate size. By means of equation (7) the corresponding effective aggregate size is found to vary from *87* to *30 nm* as demonstrated in Fig 5. Fig 6. presents a plot of $tan\delta$ as a function of polarising field, *H*, for the sample under test. Whilst the frequency at which $tan\delta$ is a maximum increases with increase in polarising field the amplitude at this frequency decreases and is indicative of the fluid becoming less-lossy with increase in *H*.

As from equation (12), the heat dissipation in the sample, *T*, is seen to be a function of $\chi''(\omega)$, this function will also have a similar profile to that of Fig 6, for varying values of polarising field. The dissipation arises from the orientational relaxation of the particles. Fig 7. shows six plots of $\chi'(\omega, H)$ and $\chi''(\omega, H)$ against *f,* obtained for sample 2, with *H*, being varied from *0* up to *+13.6 kA/m* and back down to *0*; the approximate values of *H* used being were, *0, 2.7kA/m, 5.5 kA/m, 8.2 kA/m, 10.9 kA/m* and *13.6 kA/m.* From this figure it is apparent that there is very little difference between the profiles of $\chi'(\omega, H)$ and also those of $\chi''(\omega, H)$ at each value of *H,* indicating that the cyclic variation of the polarising field has not introduced any hysteresis into the sample. Figs. 8 shows the corresponding results obtained for the polarizing field, *H*, being varied from *0* down to *-13.6 kA/m* and back up to *0 kA/m*; again it is apparent that there is little difference between the susceptibility profiles. Thus it is clear, that over the complete cycle of polarisition, the fluid apparently remains unaltered. Thus in terms of the proposed model, we recall that, for the magnetic fluid to be isotropic, $\chi'(\omega, H) = \chi'(\omega, -H)$ and $\chi''(\omega, H) = \chi''(\omega, -H)$; this fact is demonstrated by the examples in Figs. 7 and 8 where the plots are symmetrical about the vertical axis through the origin, thereby confirming that the isotropic properties of the sample have been unaffected .

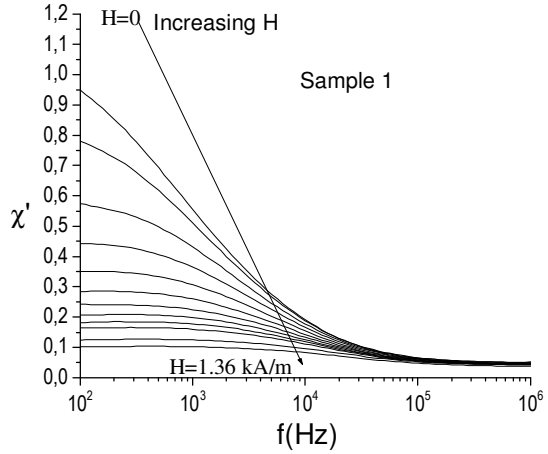

Fig 3. Plots of $\chi'(\omega, H)$ against f (Hz), for sample 1

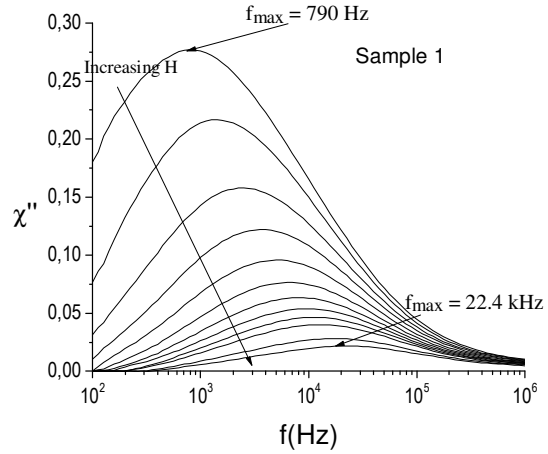

Fig 4. Plots of $\chi''(\omega, H)$ against f(Hz), for sample 1

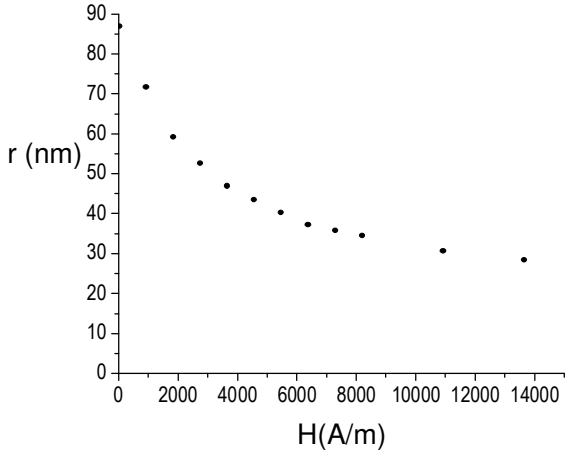

Fig 5. Plot of effective radius, r , against polarising field, H.

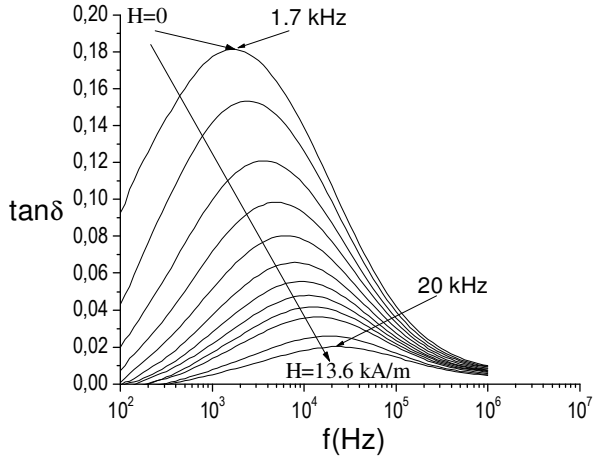

Fig 6. Plot of tanδ against polarising field, H, for sample 1.

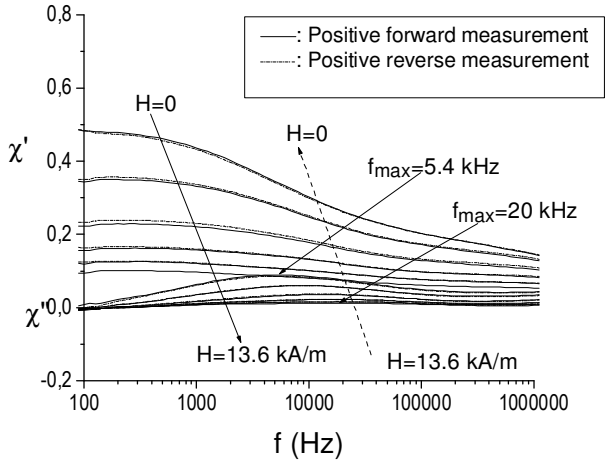

Fig 7. Plot of $\chi'(\omega, H)$ and $\chi''(\omega, H)$ (Positive forward and reverse) against f(Hz) for sample 2.

3. Summary

Measurements of the complex susceptibility, by means of the toroidal technique, of two fluid samples, sample 1 and sample 2, in the frequency range *200 Hz* to *1MHz*, as a function of polarising field are reported. In the case of sample 1, the unpolarised sample was found to have a Debye type profile with the maximum value of the $\chi''(\omega)$ component occurring at a frequency of f_{max} = *790 Hz*, corresponding to an average particle radius of *87 nm*; this value being consistent with the presence of aggregation.

The effect of applying a polarising field over the range *0-13.6 kA/m* was to shift the value of f_{max} from *790 Hz* to *13.6 kHz*, corresponding to a change in aggregate radius from *87 nm* to *28 nm*

and as (from equation (6)) the relaxation time is proportional to r^3, there is a corresponding decrease in the effective relaxation time, τ_B.

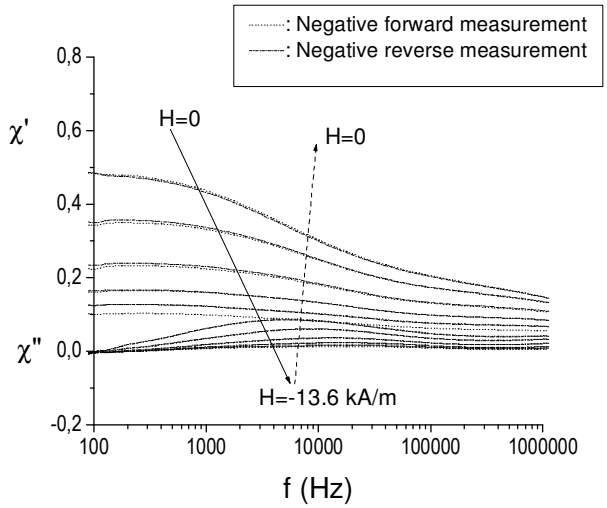

Fig 8. Plot of $\chi'(\omega, H)$ and $\chi''(\omega, H)$ (Negative forward and reverse) against f(Hz) for sample 2.

Data on the loss tangent of the sample, $\tan\delta$, and its dependence on polarising field, has also been investigated. It has been demonstrated, how, as the frequency at which $\tan\delta$ is a maximum increases with increase in polarising field the amplitude at this frequency decreases and is indicative of the fluid becoming less-lossy with increase in *H*.

In the case of sample 2, measurements were made to determine if the application of a polarizing field to a magnetic fluid would have any permanent effect on its isotropic properties upon removal of the field.

In this case the polarizing field, *H*, was varied from *0* up to *+13.6 kA/m* back down to *0*, down to *-13.6 kA/m* and back up to *0 kA/m* and from plots of both $\chi'(\omega, H)$, vs *H* and $\chi''(\omega, H)$, it was found that this cyclic variation in *H* did not effect the isotropic properties of the fluid sample.

Acknowledgement

Acknowledgement is due to Prof. B.K.P.Scaife for useful discussions and also to the European Space Agency (ESA) for the funding of this work.

References

[1] Rosensweig, R.E., Nestot, J.W., and Timmins, R.S., AIChE Chem.Eng.Sym. 5, London, (1965)104-118;133-137.

[2] Debye, P., Polar Molecules, New York, The Chemical Catalog Company Ltd. (1929)

[3] Maiorov, M.M., Magnetohydrodynamics (cover-to-cover translation of Magnitnaia Hidrodinamika) (1979) 2, 21, 135.

[4] Fannin, P.C., Scaife, B.K.P., and Charles, S.W., J. Magn. Magn. Mater.,72 (1988) 95.

[5] Fannin, P.C., J.Mol.Liq., 69 (1996)39.

[6] Brown, W.F., J. Appl. Phys. 34 (1963) 1319.

[7] Neel, L., Ann. Geophys. 5 (1949) 99.

[8] Charles, S.W., Chem.Eng. Comm., 67(1988) 145.

[9] De Gennes, P.G., and Pincus, P.A., Phys. Kondens. Materie 11(1970)189.

[10] Socoliuc, V., Rasa, M., Sofonea, V., Bica, D., Osvath, L., and Luca, D., J. Magn. Magn. Mater.,191 (1999) 241.

[11] Scholten, P.C., J. Magn. Magn. Mater., 39 (1983) 99.

[12] Fannin, P.C., Scaife, B.K.P., and Charles,S.W., J.Phys.D:Appl.Phys.21(1988)533.

[13] Coffey,W.T, Cregg, P.J. and Kalmykov, Yu.P. , 'Advances in Chemical Physics', Editors I.Prigogine and S.A.Rice, vol LXXXIII. (John Wiley & Sons Inc). (1993) 263.

[14] Fannin,P.C, and Raikher, Yu.L, J.Phys.D:Appl.Phys.34 (2001) 612.

[15] Bottcher, C.J.F., Theory of Electric Polarisation, Amsterdam, Elsevier Publishing Company, (1952)

[16] Fannin,P.C. and Charles, S.W, J.Magn.Magn.Mater. 226 (2001)1887.

[17] Scaife, B.K.P., Principles of Dielectrics, Oxford; Clarendon Press (1989)

[18] Rosensweig, R.E., J.Magn.Magn.Mater. 252 (2002) 370.

[19] Jeffreys, H and Jeffreys, B.S, " Weierstrass Theorem on Approximation by Polynomials", in "Methods of Mathematical Physics", 3rd ed. Cambridge University Press (1988) 446-448.

[20] Fannin, P.C., and C.Mac Oireachtaigh in press, J. Magn. Magn. Mater.

[21] Fannin, P.C., Scaife, B.K.P., and Charles, S.W., J.Phys.E:Sci. Instrum, 19 (1986)238.