

## INVESTIGATION OF THE NON-LINEAR AND ISOTROPIC PROPERTIES OF MAGNETIC FLUIDS

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### Abstract

Measurement of the frequency dependent, complex susceptibility,  $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ , of magnetic fluids, by means of the toroidal technique, is a well established technique for determining the dynamic properties of magnetic fluids. Here we further demonstrate its usefulness in investigating (1) the non-linear and (2) the isotropic properties of magnetic fluids under the influence of an external polarising field. In the case of a fluids isotropic properties we show how data, obtained from such polarised measurements, in conjunction with the Weierstrass hypothesis, can be used to determine the isotropic properties of a sample. We also show how the magnetic analogue of the non-linear model of Déjardin, may be used to describe the susceptibility spectra of magnetic fluids with values of polarizing fields up to 2,250 A/m.

**Keywords:** Complex susceptibility; Relaxation; Non-linear; Isotropic properties ; Magnetic fluids.

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### 1. Introduction.

A ferrofluid is a colloidal suspension of single domain ferromagnetic particles dispersed in a liquid carrier and stabilised by means of a suitable organic surfactant. The particles have radii ranging from approximately 2-10 nm and when they are in suspension their magnetic properties can be described by the Paramagnetism theory of Langevin, suitably modified to cater for a distribution of particle sizes. The particles are considered to be in a state of uniform magnetisation with a magnetic moment,  $m$ , given by:  $m = M_s v$ , where  $M_s$  denotes saturation magnetisation and  $v$  is the magnetic volume of the particle.

The normalized magnetisation  $M/M_s$  is described by the Langevin expression,

$$M/M_s = [\coth \xi - 1/\xi] = L(\xi) \quad (1)$$

where

$$L(\xi) = \xi/3 - \xi^3/45 + \xi^5/945 - \dots, \quad (2)$$

$\xi = mH_0/kT$ , where  $k$  is Boltzmanns constant and  $H_0$  the magnetizing field.

Thus  $L(\xi)$  is a function of  $H_0$ ,  $H_0^3$ ,  $H_0^5$  etc. which give rise to the non-linear properties of the samples.

There are two distinct mechanisms by which the magnetisation of ferrofluids may relax after an applied field has been removed: either rotational Brownian motion of the particle within the carrier liquid, with its magnetic moment,  $m$ , locked in an axis of easy magnetisation, or by rotation of the magnetic moment within the particle. The time associated with the rotational diffusion is the Brownian relaxation time  $\tau_B$  [1] where

$$\tau_B = 3 V \eta / k T \quad (3)$$

$V$  is the hydrodynamic volume of the particle and  $\eta$  is the dynamic viscosity of the carrier liquid.

In the case of the second 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 probability of such a transition is  $\exp(-\sigma)$  where  $\sigma$  is the ratio of anisotropy energy to thermal energy ( $Kv/kT$ ). This reversal time is characterised by a time  $\tau_N$ , which is referred to as the Néel relaxation time [2], and given by the expression,

$$\tau_N = \tau_0 \exp(\sigma) \quad (4)$$

$\tau_0$  is a decay time, often quoted as having an approximate value of  $10^{-8}$  to  $10^{-10}$  s.

For the particle sizes used in this study, Néel relaxation would be observed in the MHz-GHz region; thus in the frequency range measured here Brownian relaxation is considered to be dominant.

## 2. Susceptibility

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

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

According to Debye's theory [3] the complex susceptibility,  $\chi(\omega)$ , has a frequency dependence given by the equation,

$$\chi(\omega) - \chi_\infty = (\chi_0 - \chi_\infty) / (1 + i\omega\tau_{eff}) \quad (6)$$

$$= (\chi_0 - \chi_\infty) ( 1 / (1 + \omega^2 \tau_{eff}^2) - i \omega \tau_{eff} / (1 + \omega^2 \tau_{eff}^2) ) \quad (7)$$

where  $\chi_\infty$  indicates the susceptibility value at very high frequencies and  $\chi_0$  is the static or low frequency susceptibility, and is defined as

$$\chi_0 = nm^2/3kT\mu_0 \quad (8)$$

$n$  is the particle number density,  $k$  is Boltzmann's constant and  $T$  the temperature.  $\tau_{eff}$  is the effective relaxation time which, over the frequency range measured here, in this case is considered to be dominated by the Brownian relaxation time  $\tau_B$ , where it may also be determined from,

$$\tau_B = 1/\omega_{max} = 1/2\pi f_{max}, \quad (9)$$

where  $f_{max}$  is the frequency at which  $\chi''(\omega)$  is a maximum.

The relation between  $\chi'(\omega)$  and  $\chi''(\omega)$  and their dependence on frequency,  $\omega/2\pi$ , can be displayed by means of the magnetic analogue of the Cole-Cole plot [4] where the data fits a depressed circular arc. In the Cole-Cole case the circular arc cuts the  $\chi'(\omega)$  axis at an angle of  $\alpha_c\pi/2$ ;  $\alpha_c$  is referred to as the Cole-Cole parameter and is a measure of the particle-size distribution.

The magnetic analogue of the Cole-Cole circular arc is described by the equation

$$\chi(\omega) = \chi_\infty + (\chi_0 - \chi_\infty) / (1 + (i\omega\tau)^{1-\alpha_c}), \quad 0 < \alpha_c < 1 \quad (10)$$

which for  $\alpha_c = 0$ , reduces to that of equation (6).

### 3. Non-linear susceptibility.

The non-linear behaviour of the susceptibility of a magnetic fluid [5] is due to the nature of its magnetisation curve, i.e its Langevin profile, the slope of which is the incremental susceptibility,  $\Delta\chi(\omega)$ , and whose value decreases with increasing polarising field, as illustrated in Fig 1 which shows a typical magnetization curve for a ferrofluid sample.

The linear region of a magnetization curve is considered to be the field range in which the tangent of the curve, which determines the susceptibility, given by  $\chi = dM/dh_a$ , does not significantly change, as indicated by A in Fig 1. This is the low field region, usually below 1 kA/m for typical ferrofluids. Beyond this range non-linearity gradually becomes significant as the slope of the magnetization curve gradually decreases as indicated by points B, C and D.

In direct analogy with the dielectric case,  $\Delta\chi(\omega)$ , is defined as the difference between the susceptibility value measured in the presence ( $\chi(\omega)_H$ ) and absence ( $\chi(\omega)_{H=0}$ ) of an external potential with  $\Delta\chi(\omega) = \chi_H(\omega) - \chi_{H=0}(\omega)$ , which can also be represented in the complex form,  $\Delta\chi(\omega) = \Delta\chi'(\omega) - i\Delta\chi''(\omega)$ .

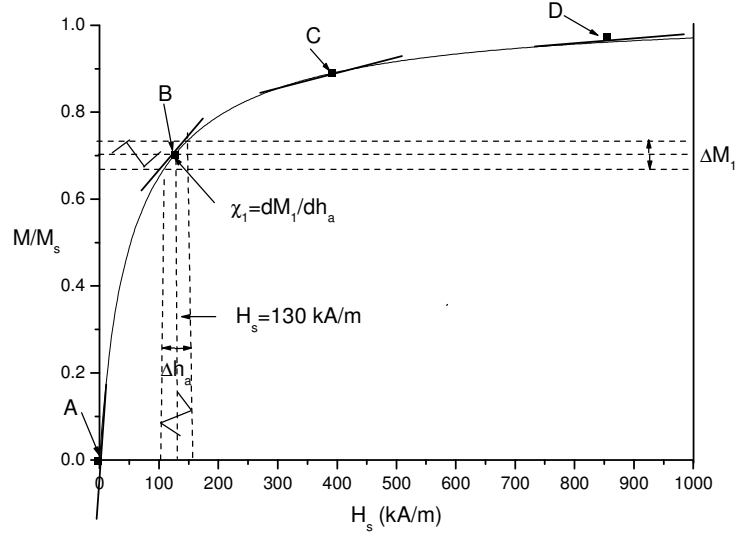


Fig 1. Magnetisation curve of ferrofluid sample.

In the investigation of the non-linear properties of dielectrics Coffey and Paranjape [6] derived a theory for nonlinear relaxation in dielectric systems, the magnetic analogue of which, as shown here, can be easily applied for the case of ferrofluids.

We considered the case where an external potential, comprising a strong biasing and a relatively small alternating field ( $H_0/H_s \ll 1$ ) are superimposed, giving a total field  $H(t) = H_s + H_0 \cos(\omega t)$ . In this case the solution for  $\chi$  is given by the expression [5, 6], where,

$$\chi'(\omega, H_s) = \frac{N\mu_m^2}{3\mu_0 k_B T} \frac{1}{1 + \omega^2 \tau_B^2} \left[ 1 + \left( \frac{\mu_m H_s}{k_B T} \right)^2 \frac{(2\omega^4 \tau_B^4 - \omega^2 \tau_B^2 - 27)}{15(1 + \omega^2 \tau_B^2)(9 + \omega^2 \tau_B^2)} \right] \quad (11)$$

$$\chi''(\omega, H_s) = \frac{N\mu_m^2}{3\mu_0 k_B T} \frac{\omega \tau_B}{1 + \omega^2 \tau_B^2} \left[ 1 - \left( \frac{\mu_m H_s}{k_B T} \right)^2 \frac{(\omega^4 \tau_B^4 + 19\omega^2 \tau_B^2 + 42)}{15(1 + \omega^2 \tau_B^2)(9 + \omega^2 \tau_B^2)} \right] \quad (12)$$

One can readily see that both of the above equations consist of a Debye component (Eqn. 7) together with a second component which is the non-linear component.

The non-linear terms of Eqs. (11) and (12) are regarded as the increment of the susceptibility,  $\Delta\chi$ , due to the nonlinear response, thus we may write

$$\Delta\chi'(\omega, H_s) = \frac{\chi_0}{1 + \omega^2 \tau_B^2} \left( \frac{\mu_m H_s}{k_B T} \right)^2 \frac{(2\omega^4 \tau_B^4 - \omega^2 \tau_B^2 - 27)}{15(1 + \omega^2 \tau_B^2)(9 + \omega^2 \tau_B^2)} \quad (13)$$

$$\Delta\chi''(\omega, H_s) = \frac{\chi_0 \omega \tau_B}{1 + \omega^2 \tau_B^2} \left( \frac{\mu_m H_s}{k_B T} \right)^2 \frac{(\omega^4 \tau_B^4 + 19\omega^2 \tau_B^2 + 42)}{15(1 + \omega^2 \tau_B^2)(9 + \omega^2 \tau_B^2)} \quad (14)$$

The term  $\Delta\chi$  is the susceptibility difference between a polarised and an unpolarised measurement; it may also be represented in its complex form of  $\Delta\chi = \Delta\chi' - i\Delta\chi''$ .

The above expressions for non-linear susceptibility refer to the mono-dispersed case. To apply them to a realistic system we have to introduce  $\chi_\infty$  into the expressions, and to account for the particle distribution. If the Cole-Cole parameter  $\alpha$  is used, the following expression, as proposed by Déjardin [7] for the increment of the non-linear susceptibility,  $\Delta\chi$ , is arrived at, where,

$$\Delta\chi(\omega, H_s) = \frac{\chi_0}{(1 + (i\omega\tau_B)^{1-\alpha})} \frac{\mu_m H_s}{k_B T} \frac{1 + (1 + (i\omega\tau_B)^{1-\alpha})(2 + \frac{1}{3}(i\omega\tau_B)^{1-\alpha})}{15(1 + (i\omega\tau_B)^{1-\alpha})(1 + \frac{1}{3}(i\omega\tau_B)^{1-\alpha})} \quad (15)$$

For  $\alpha=0$  the latter equation is the complex form of the non-linear increment of susceptibility, Eqs. (13) and (14).

#### 4. Measurement Technique.

Complex magnetic susceptibility measurements, over the approximate frequency range 100 Hz to 1 MHz, were made by means of the toroidal technique [8] in conjunction with a Hewlett Packard RF Bridge 4291A. 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.

In the case of non-linear measurements H was varied from 0 to 3.75 kA/m on a 100 G colloidal suspension of magnetite in water whilst in the case of isotropic measurements H was varied from 0 to  $\pm 13.6$  kA/m on a 110 G colloidal suspension of magnetite in water.

The values of the  $H_s$  used were 750 A/m, 1.5 kA/m, 2.25 A/m, 3 kA/m and 3.75 kA/m and from inspection of the fluids magnetization curve it was determined that the first value of  $H_s$  operated in the linear region whilst the remainder operated in the non-linear region. Here we present the results obtained in the 750 A/m case (linear) and in the 3.25 kA/m case (non-linear).

#### 5. Non-Linear measurements.

Here we will show just two of the five polarizing field measurements made, namely the contrasting results obtained for the 750 A/m and 3250 A/m fields. The measured susceptibility components and fits are presented in Fig. 2(a) for the case of 750 A/m field.

The form of the fitting equation used is the same as Eqs. (11) and (12), with the Cole-Cole parameter  $\alpha$  included (we also add in the high frequency susceptibility term,  $\chi_\infty$ ),

$$\chi(\omega, H_s) = \frac{\chi_0 - \chi_\infty}{1 + (i\omega\tau_B)^{1-\alpha}} \left[ 1 - \left( \frac{\mu_m H_s}{k_B T} \right)^2 \frac{1 + (1 + (i\omega\tau_B)^{1-\alpha})(2 + \frac{1}{3}(i\omega\tau_B)^{1-\alpha})}{15(1 + (i\omega\tau_B)^{1-\alpha})(1 + \frac{1}{3}(i\omega\tau_B)^{1-\alpha})} \right] + \chi_\infty \quad (16)$$

We fit simultaneously the polarised curve (lower curve of Fig. 2 (a) with Eq. (16) and the unpolarised data with the usual Cole-Cole equation. The Brownian relaxation time of the unpolarised data was estimated to be  $\tau_B = 1.3 \times 10^{-4}$  s and the  $\alpha$  parameter was 0.45. The incremental deviation of the static susceptibility,  $\Delta\chi_0$ , in this instance is calculated as  $\Delta\chi_0 = -0.02$ . The small deviation between the unpolarised data and the polarised data is plotted in Fig. 2 (b), in which the fit for  $\Delta\chi$  is obtained by use of Eq. (15). The corresponding Cole-Cole diagram is the inset graph.

Increasing the biasing field up to 2.25 kA/m it is found that the fit is still close to the data. A further increase ( $H_s > 3$  kA/m) results in the polarised susceptibility deviating widely from the un-polarised susceptibility.

The  $\chi$  and  $\Delta\chi$  curves which correspond to the 3.75 kA/m polarizing field are presented in Fig. 3(a-b). Now, we are fully into the non-linear region. Here the increment  $\Delta\chi_0$  is much larger than with the previous field (750 A/m). The  $\alpha$  parameter and moment  $\mu_m$ , used here, are the same as the previous field. The relaxation time of the polarised data is  $\tau_B = 7.2 \times 10^{-4}$  s. In this case Eq. (16) cannot describe the non-linear effect anymore, because the non-linear term becomes comparable to the linear term. This is shown in Figs. 3(a) in which a ‘‘hump’’ appears as indicated by the arrows.

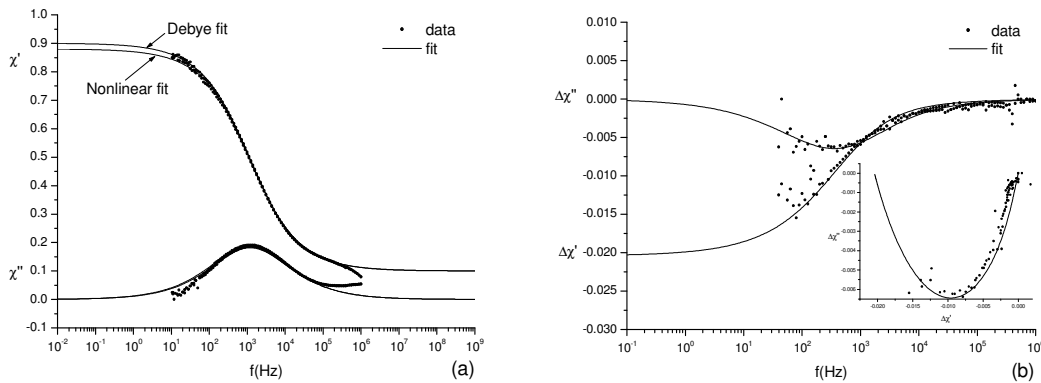


Fig 2. (a) Plot of  $\chi'(\omega)$  and  $\chi''(\omega)$  for unpolarised and 750 A/m data together with fits; (b) Plot of  $\Delta\chi'(\omega)$  and  $\Delta\chi''(\omega)$  with fits and Cole-Cole insert.

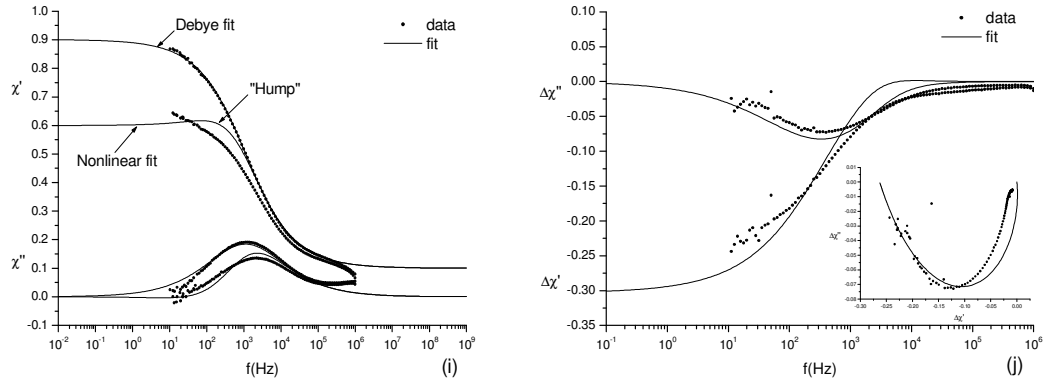


Fig 3. (a) Plot of  $\chi'(\omega)$  and  $\chi''(\omega)$  for unpolarised and 3750 A/m data together with fits; (b) Plot of  $\Delta\chi'(\omega)$  and  $\Delta\chi''(\omega)$  with fits and Cole-Cole insert.

## 6. Isotropic Measurements.

Determination of the isotropic properties may be realized through the measurement of  $\chi(\omega, H) = \chi'(\omega, H) - i\chi''(\omega, H)$ , of the fluids, by means of the toroidal technique as in the case of the non-linear measurements. The model used is based on the Weierstrass hypothesis [9] which essentially states that for a fluid to be isotropic plots of  $\chi'(\omega, H)$ , vs  $H$  and  $\chi''(\omega, H)$  vs  $H$ , should be symmetrical about the vertical axis.

Here this is achieved by measuring the fluids complex susceptibility for a cyclic variation of  $H$ : i) from 0 up to +13.6 kA/m back down to 0; ii) down to -13.6 kA/m and back up to 0 kA/m; iii) over the frequency range, 100 Hz to 1 MHz.

The approximate values of  $H$  used being, 0, 2.7kA/m, 5.5 kA/m, 8.2 kA/m, 10.9 kA/m and 13.6 kA/m.

### 6.1. Results of Isotropic Measurements.

Fig 4. shows the results obtained over the polarizing field range 0-13.6-0 kA/m; the results obtained over the range 0- -13.6-0 proved to be almost identical.

As has been previously mentioned, for the magnetic fluid to be isotropic, the condition  $\chi(\omega, H) = \chi(\omega, -H)$  and  $\chi'(\omega, H) = \chi'(\omega, -H)$ , must hold; this fact is demonstrated by the following examples in: i) Figs 5(a) and 5(b) which show the  $\chi'$  and  $\chi''$  data as a function of  $H$  at a frequency of 500Hz, ii) Figs 6(a) and 6(b) show the  $\chi'$  and  $\chi''$  data as a function of  $H$  at a frequency of 5kHz, iii) Figs 7(a) and 7(b) show the  $\chi'$  and  $\chi''$  data as a function of  $H$  at a frequency of 10kHz.

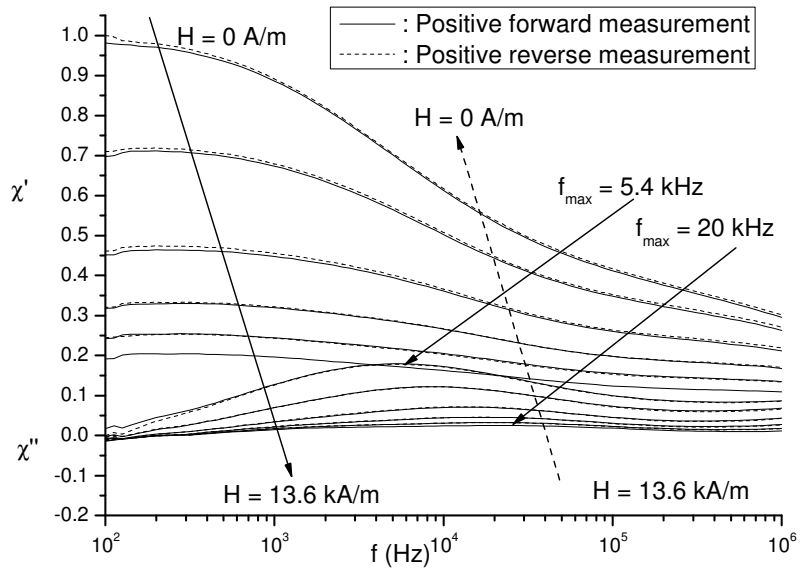


Fig 4. Plot of  $\chi'(\omega, H)$  and  $\chi''(\omega, H)$  (Positive forward and reverse) against  $f$  (Hz)

In all of the above cases, these plots are shown fitted to a 9<sup>th</sup> order polynomial and from inspection of the corresponding resulting odd coefficients one can determine how good an approximation is made to equation (16).

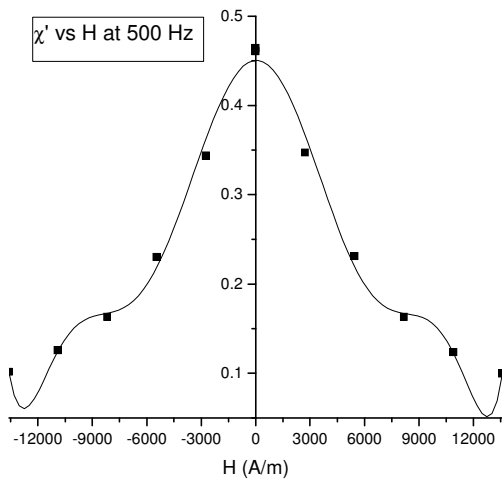


Fig 5(b) Fit to  $\chi'$  against  $H$  data at 500 Hz.

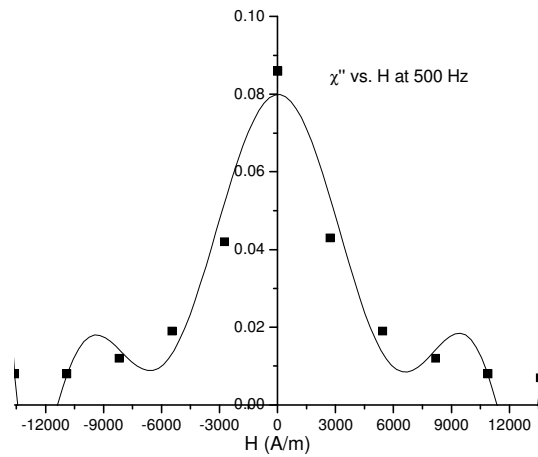


Fig 5(b) Fit to  $\chi''$  against  $H$  data at 500 Hz.



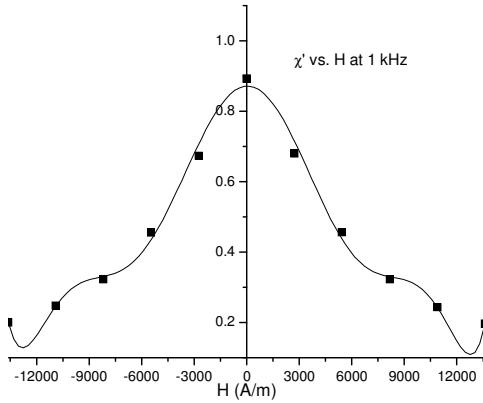


Fig 6(a) Fit to  $\chi'$  against H data at 1000 Hz.

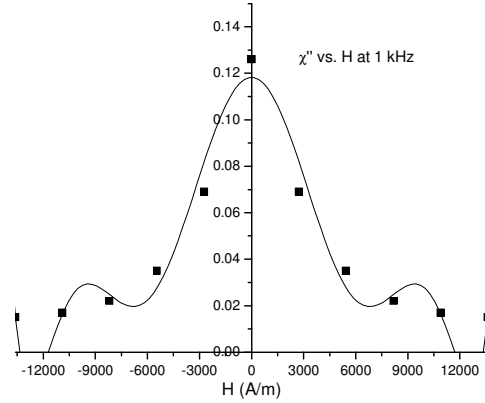


Fig 6(b) Fit to  $\chi''$  against H data at 1000 Hz.

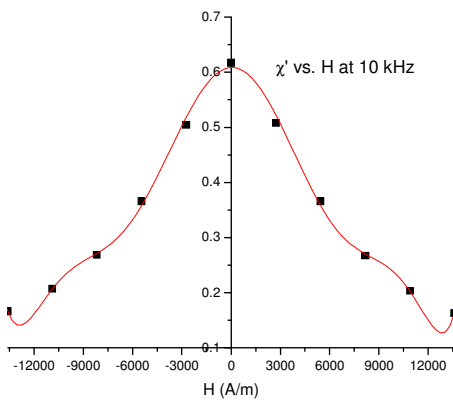


Fig 7(a) Fit to  $\chi'$  against H data at 10 kHz.

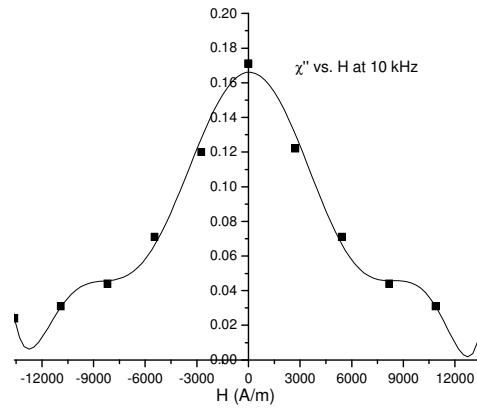


Fig 7(b) Fit to  $\chi''$  against H data at 10 kHz.

Thus these results clearly demonstrate, that in all the examples given, the plots are symmetrical about the vertical axis through the origin, thereby confirming that the isotropic properties of the sample have been unaffected by the application of a cyclic polarizing field.

## 7. Overall Conclusions.

The object of this work was two-fold,

- 1) to investigate the non-linear behaviour of the susceptibility of a magnetic fluid, and
- 2) to study the possible influence which the application of a cyclic polarizing field to a magnetic fluid would have on its isotropic properties.

For 1) we demonstrated that the modified model of Déjardin, may be used to describe the susceptibility spectra of magnetic fluids with values of  $H_S$  up to 2,250 A/m.

For 2) Plots of  $\chi'(\omega, H)$ , vs  $H$  and  $\chi''(\omega, H)$  vs  $H$ , were shown to be symmetrical about the vertical axis, thereby satisfying the Weierstrass hypothesis and confirming that the cyclic variation in  $H$  had negligible 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. Thanks are also due to A.T. Giannitsis.

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