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On the utility of low frequency, polarised, complex susceptibility measurements in the investigation of the dynamic properties of magnetic fluids

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ABSTRACT

The measurement of the field and frequency-dependent, complex susceptibility, $\chi(\omega, H) = \chi'(\omega, H) - i\chi''(\omega, H)$, is an established method for investigating the dynamic properties of magnetic fluids. Polarised measurements have been used to investigate many properties of magnetic fluids, including, relaxation mechanisms, aggregation, magnetic losses, loss factor tanδ, power factor sinδ, and the influence which polarising fields may have on the hysteresis and isotropic properties of samples.
In this paper, a review is given of these topics and typical results are presented.

1. Introduction

Magnetic fluids consist of colloidal suspensions of nanoparticles of ferromagnetic or ferrimagnetic materials dispersed in a carrier liquid and stabilized 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),

$$m = M_s v \quad (1)$$

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,

$$M = M_s[\coth\xi - 1/\xi] \quad (2)$$

where $L(\xi) = \xi/3 - \xi^3/45 + \xi^5/945 + \ldots$, and $\xi = mH/kT$, where k is Boltzmann's constant T is temperature and H is the magnetizing field.

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

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,

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega). \quad (3)$$

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,

$$\chi(\omega) = (\chi_0 - \chi_\infty)/(1 + i\omega\tau) + \chi_\infty \quad (4)$$

where the static susceptibility

$$\chi_0 = nm^2/3kT\mu_0. \quad (5)$$

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 is the relaxation time and μ_0 is the permeability of free space.

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A typical Debye type spectrum is shown in Fig. 1a) where the loss, or $\chi''(\omega)$ component, displays a peak (at a frequency f_{max}), whose value cannot be greater than $\chi_0/2$.

However, the Debye model assumes that the ferrofluid consists of mono-dispersed particles, and as this is not the case, one would expect the profile of a samples spectrum to differ from that of Fig. 1a). This is illustrated in Fig. 1b), which shows the effect of incorporating a normal distribution of radii, of standard deviation, σ_r, into the Debye model. These results show the $\chi'(\omega)$ component inclining from the vertical position, and the peak of the $\chi''(\omega)$ component reducing as the absorption curve become broader.

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, whereby the magnetic moment must overcome the particles anisotropy energy barrier and is known as the Néel relaxation process with relaxation time τ_N [7].

The Brownian relaxation time τ_B is given by [6]

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

where r is the hydrodynamic radius of the particle, η is the dynamic viscosity of the carrier liquid.

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

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

Thus by determining f_{max} from Eq. (7) we are enabled 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].

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. This reversal time may be described approximately in terms of Brown's [12] expressions for high and low barrier heights, as,

$$\begin{aligned} \tau_N &= \tau_0 \sigma^{-1/2} \exp(\sigma), \quad && \sigma \geq 2 \\ &= \tau_0 \sigma, && \sigma << 1. \end{aligned} \tag{8}$$

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

Magnetic fluids have a distribution of particle sizes and have an effective relaxation time τ_{eff} [13], which in terms of τ_B and τ_N, is given by,

$$\tau_{eff} = \tau_N \tau_B / (\tau_N + \tau_B), \tag{9}$$

the mechanism with the shortest relaxation time being dominant. τ_{eff} is related to the frequency f_{max} of the maximum of the $\chi''(\omega)$ component, by the expression,

$$\tau_{eff} = 1/2\pi f_{max}. \tag{10}$$

In the case where $\tau_N >> \tau_B$,

$$\tau_{eff} = 1/2\pi f_{max} = \tau_B = 4\pi\eta r^3/kT. \tag{11}$$

An indication of the spectrum of relaxation times likely to be encountered in a typical magnetic fluid is given in [14]. It is shown, as in Fig. 2a), that, for particle sizes which range from 1.44 to 12.2 nm, those with radii greater than 6 nm the dominant relaxation mechanism is Brownian whilst those with radii less than 6 nm the Néel mechanism is dominant.

Fig. 2b) is a plot of the corresponding values of f_{max} for the particle sizes used together with three further particle sizes of 17, 22, and 28 nm, respectively; these latter three sizes being included in order to cater for the possible presence of aggregation. The figure clearly shows that Néel relaxation would be observed in the approximate frequency range of 10^5 Hz upwards, whilst Brownian is the dominant mechanism below 10^5 Hz.

For a distribution of particle sizes, a distribution of relaxation times, τ, will exist and the Cole-Cole parameter, α [15], is a useful parameter in determining the distribution of relaxation times. In the Cole-Cole case, where the complex susceptibility data fits a depressed circular arc, 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 [15]. In the Cole-Cole case the circular arc cuts the $\chi'(\omega)$ axis at an angle of $\alpha\pi/2$; α 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 Eq. (12), where,

$$\chi(\omega) = \chi_\infty + (\chi_0 - \chi_\infty)/\left[1 + (i + \omega\tau)^{1-\alpha}\right], \quad 0 < \alpha < 1 \tag{12}$$

which for $\alpha = 0$, reduces to that of Eq. (4).

1.1. Field dependence

From the Langevin function for the magnetization of the fluid, Eq. (2) for the samples presented here, an expression for the field dependence of the frequency dependent susceptibility, $\chi(\omega, H)$, can be written as follows [16],

$$\chi(\omega, H) = \frac{\chi_0(1 + f(H)) - \chi_\infty}{1 + i\omega\tau_{eff}} + \chi_\infty \tag{13}$$

with,

$$(1 + f(H)) = 3\left[1 + \left(\frac{kT}{mH}\right)^2 - \coth^2\left(\frac{mH}{kT}\right)\right] \tag{14}$$

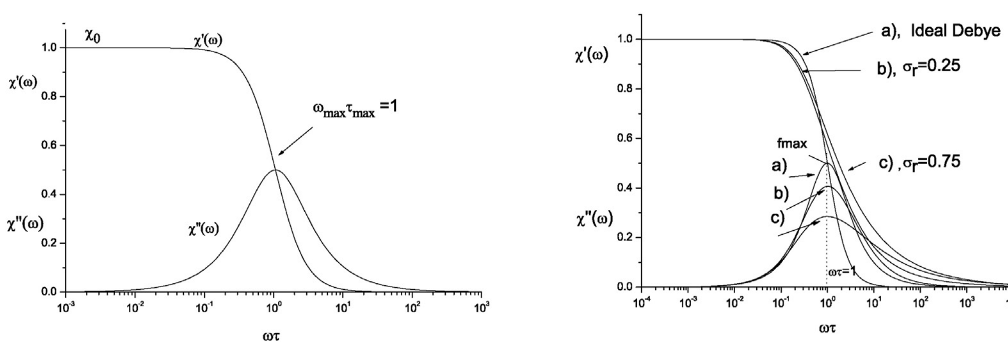

Fig. 1. a) Debye type profile, plot of $\chi'(\omega)$ $\chi''(\omega)$ against $\omega\tau$. b) Debye type profiles (including plots in A) and normal distribution of particle radii, σr) of $\chi'(\omega)$ and $\chi''(\omega)$ against $\omega\tau$.