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Complex susceptibility measurements of magnetic fluids over the frequency range 50 MHz to 18 GHz

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Abstract. We report on the measurement, over the frequency range 50 MHz to 18 GHz, of the complex susceptibility, $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$, of a magnetic fluid as a function of the polarizing field. Measurements were obtained by means of the short-circuit transmission line technique, with the frequency range being realized by the use of an HP Network Analyser which operates up to 40 GHz. From these measurements more complete $\chi'(\omega)$ and $\chi''(\omega)$ profiles have been obtained, from which the values of resonant frequency, f_{res}, and frequency of maximum absorption, f_{max}, can be identified. The variation in f_{max}/f_{res} as a function of the polarizing field, H, over the range 0–100 kA m^{-1}, was investigated and found to be in accordance with that predicted by Raikher and Shliomis. The extended susceptibility profiles have enabled the normalized after-effect function of the sample, $b(t)/b(0)$, to be investigated within the 10^{-11} s time region.

1. Introduction

We have previously discussed [1, 2] the use of transmission line techniques for the measurement of the complex susceptibility up to a frequency of 6 GHz, the upper frequency limit being due to the frequency limitations of the measuring equipment, the HP 8753C Network Analyser. This paper describes measurements up to a frequency of 18 GHz, made using the HP 8722D Network Analyser; however, in this instance the upper frequency is imposed by the limitations of the coaxial cell used and not by the analyser, which has an upper frequency of 40 GHz.

Under equilibrium conditions, the magnetic moment, m, 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. In the case where the polar angle θ is small, the angular resonant frequency, ω_0, is given by [3]

$$\omega_0 = \gamma H_A \tag{1}$$

where γ is the gyromagnetic ratio.

The internal field H_A (A m^{-1}) for a particle with uniaxial anisotropy has magnitude

$$H_A = 2K/M_s \tag{2}$$

where M_s (T) is the saturation magnetization per unit volume.

The existence of a resonance phenomenon can be determined from measurement of the complex susceptibility, $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$, of the suspension, this effect being indicated by a transition in the value of $\chi'(\omega)$ from a positive to a negative quantity at an angular frequency $\omega_{res} = 2\pi f_{res}$.

The distributions of particles commonly used in ferrofluids have radii ranging from approximately 2–10 nm, and as these particles are single domain they are considered to be in a state of uniform magnetization with magnetic moment, m, given by

$$m = M_s v \tag{3}$$

where v is the particle volume.

The complex components of the susceptibility, $\chi(\omega)$, of an assembly of single domain particles can be described in terms of the Kramers–Kronig relations [4, 5], with

$$\chi'(\omega) = \chi_\infty + \left(\frac{2}{\pi}\int_0^\infty \frac{\chi''(u)u}{u^2 - \omega^2}\,du\right) \tag{4a}$$

and

$$\chi''(\omega) = -\left(\frac{2\omega}{\pi}\int_0^\infty \frac{\chi'(u) - \chi_\infty}{u^2 - \omega^2}\,du\right) \tag{4b}$$

where χ_∞ is the susceptibility at infinite frequency.

The variable of integration, u, is real and the principal parts of the integrals are to be taken in the event of singularities of the integrands.

$\chi(\omega)$ may also be described in terms of its parallel, $\chi_\parallel(\omega)$, and perpendicular, $\chi_\perp(\omega)$, components, with

$$\chi(\omega) = \left(\chi_\parallel(\omega) + 2\chi_\perp(\omega)\right)/3 \tag{5}$$

and where the corresponding relaxation times are $\tau_\parallel$ and $\tau_\perp$, respectively.

The parallel susceptibility, $\chi_\parallel(\omega)$, is purely relaxational in character and can be described by the Debye equation [6], with

$$\chi_\parallel(\omega) = \frac{\chi_\parallel(0)}{1 + \mathrm{i}\omega\tau_\parallel} \tag{6}$$

and where $\chi_\parallel(0)$ is the static parallel susceptibility and $\tau_\parallel$ is considered to be equal to the Néel relaxation time τ_N [7, 8].

$\tau_\parallel$ is related to the frequency f_{max} at which the imaginary component of $\chi''(\omega)$ is at a maximum by the expression

$$f_{max} = 1/(2\pi\tau_\parallel). \tag{7}$$

The transverse susceptibility, $\chi_\perp(\omega)$, which is associated with resonance, may be described in its complex form by equations derived in [3].

The after-effect function, $b(t)$, is related to the frequency dependent complex susceptibility via the dissipative component, $\chi''(\omega)$, by means of the equation [4]:

$$\frac{\chi''(\omega)}{\omega} = \frac{1}{2}\mathrm{Re}\left(\int_{-\infty}^{\infty} b(t)\exp(-\mathrm{i}\omega t)\,\mathrm{d}t\right) \tag{8}$$

which, in terms of $b(t)$, may be written as

$$\begin{aligned} b(t) &= 2\mathrm{Re}\left(\frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{\chi''(\omega)}{\omega}\exp(\mathrm{i}\omega t)\,\mathrm{d}\omega\right) \\ &= 2\mathrm{Re}\left[F^{-1}\left(\chi''(\omega)/\omega\right)\right] \end{aligned} \tag{9}$$

where F^{-1} denotes the inverse Fourier transform.

2. Measurements

The measurements reported here, over the frequency range 50 MHz to 18 GHz, were made under computer control using the HP 8722D Network Analyser with a 50 Ω line incorporating a coaxial cell. The coaxial cell containing the ferrofluid sample was placed between the pole faces of an electromagnet (the axis of the cell being perpendicular to the field), and the polarizing field, H, was varied over an increasing range of 17 values, of approximately 0, 2, 10, 16, 22, 28, 34, 41, 48, 55, 62, 68, 75, 81, 88, 95 and 100 kA m^{-1}. The sample was placed at the end of this line and a standard HP short circuit load used as the termination; automatic swept measurements (over the entire frequency range) of the input impedance of the line containing the samples were taken and from these measurements the complex components $\chi'(\omega)$ and $\chi''(\omega)$ were determined.

As with other network analysers, the instrument used in this study automatically measures the reflection and transmission characteristics of devices by the use of the scattering or 'S' parameters [9], which are a measure of the ratio of the power reflected from a device to the power incident on a device. When the instrument is operated in a one port mode it measures the S_{11} (or S_{22}) parameter. Now,

$$S_{11} = (Z_L - Z_0)/(Z_L + Z_0) \tag{10}$$

where Z_L is the load impedance and Z_0 is the characteristic impedance of the instrument. The instrument is capable of converting the S_{11} measurements into the real and imaginary components of Z_L by computing the equation

$$Z_L = Z_0(1 + S_{11})/(1 - S_{11}). \tag{11}$$

Thus, in the case of an inductive load it automatically measures the resistive component, R_L, and the reactive component, X_L, respectively.

Apart from a wider operating frequency range, this instrument has a number of advantages over other HP analysers—such as the HP 8753C, the use of which has previously been discussed by the the authors—including a low-loss flexible cable, a ratchet spanner to ensure optimum connector pressure and a more accurate calibration procedure.

3. Results and discussion

The results obtained for the suspension of magnetite particles (Fe_3O_4) in a hydrocarbon (Isopar-M) carrier are shown in figure 1. This is a normalized plot of $\chi'(\omega)$ and $\chi''(\omega)$ against $\log f$ Hz up to a frequency of 18 GHz for a sample with a saturation magnetization of 0.047 T, an average particle size of 9.4 nm (the median diameter of the log normal volume distribution), a standard deviation of 0.4 and an M_s of 0.4 T.

In the unpolarized state, the maximum of the loss-peak of $\chi''(\omega)$ occurs at a frequency $f_{max} = 1$ GHz, whilst the frequency at which $\chi'(\omega)$ becomes negative, f_{res}, is approximately 1.65 GHz.

Variation of the polarizing field over the range 0–100 kA m^{-1} results in a higher frequency of oscillation (equation (1)), and from figure 2 a linear relationship is found to exist between f_{res} and H, giving, from equation (1),

$$\omega_0 = \gamma(\overline{H}_A + H) \tag{12}$$

and thereby enabling an average value of internal anisotropy field, $\overline{H}_A$, to be determined [10]. This is shown to be approximately 48 kA m^{-1}, resulting in a corresponding average value of anisotropy constant of $\overline{K} = 9.5 \times 10^3$ J m^{-3}.

Two processes contribute to the susceptibility in the frequency range studied: namely, the transverse susceptibility, $\chi_\perp(\omega)$, associated with resonance, and the

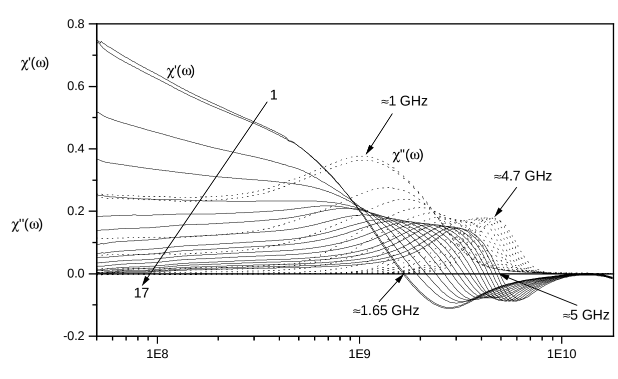

Figure 1. Plot of $\chi'(\omega)$ and $\chi''(\omega)$ against frequency in Hz, over the frequency range 50 MHz to 18 GHz, for 17 increasing values of polarizing field, of approximately 0, 2, 10, 16, 22, 28, 34, 41, 48, 55, 62, 68, 75, 81, 88, 95 and 100 kA m^{-1}, respectively.

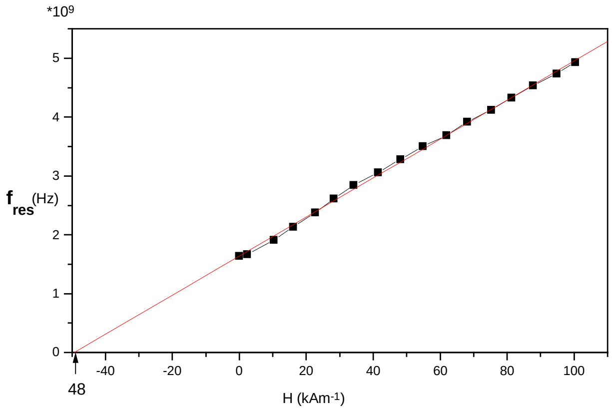

Figure 2. Plot of $f_{\rm res}$ against polarizing field, H (kA m^{-1}), with corresponding values of $\overline{H}_{\rm A} = 48$ kA m^{-1}.

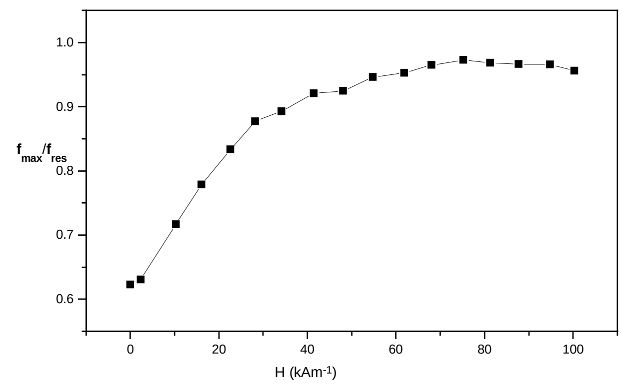

Figure 3. Plot of $f_{\rm max}/f_{\rm res}$ against polarizing field, H (kA m^{-1}).

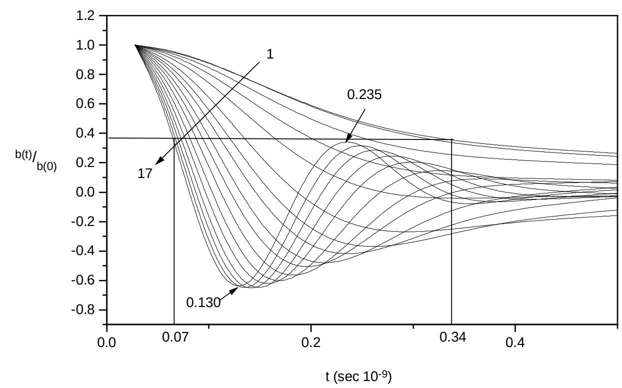

Figure 4. Plot of normalized after-effect function $b(t)/b(0)$, for 17 increasing values of polarizing field, of approximately 0, 2, 10, 16, 22, 28, 34, 41, 48, 55, 62, 68, 75, 81, 88, 95 and 100 kA m^{-1}, respectively.

parallel susceptibility, $\chi_{\parallel}(\omega)$, which is purely relaxational in character.

The transition probability between states corresponding to different easy axes of magnetization or reversal of the magnetization is a function of the ratio of the height of the potential barrier, Kv (where v is the mean particle volume of the particulate system being studied), to the thermal energy, kT. For $Kv/kT \gg 1$, corresponding to large particles in the particle size distribution, the thermal fluctuational re-orientation of the moments between easy axes is 'blocked'. Under these circumstances the weak ac field is not capable of causing any probability that the moments will surmount the energy barrier Kv, and thus the contribution of $\chi_{\parallel}(\omega)$ to the total susceptibility tends to zero. The susceptibility is thereby dominated by $\chi_{\perp}(\omega)$, i.e. the resonant component.

For $Kv/kT \ll 1$, corresponding to the smaller particles of the distribution, the susceptibility is dominated by $\chi_{\parallel}(\omega)$, i.e. by relaxation of the moments over the barrier. In this situation the system is adequately described by the Debye equation (equation (5)), with a characteristic relaxation time $\tau_{\rm N}$ given by Brown [8]

$$\begin{aligned}\tau_{\rm N} &= \tau_0 (Kv/kt)^{-1/2} \exp(Kv/kt) \qquad & Kv/kT \geqslant 2 \\ &= \tau_0 (Kv/kT) & Kv/kT \ll 1\end{aligned} \qquad (13)$$

where τ_0 is a precessional damping or extinction time and has been reported as having approximate values of between 10^{-8} and 10^{-12} s [11, 12, 13]. Here τ_0 is estimated to be approximately equal to 7×10^{-11} s.

Raikher and Shliomis [3] undertook theoretical calculations of the contribution of $\chi'_{\parallel}(\omega)$ and $\chi'_{\perp}(\omega)$ to the total susceptibility as a function of Kv/kT for different single particle-size systems. They generated profiles of $\chi'_{\parallel}(\omega)$, $\chi''_{\parallel}(\omega)$, $\chi'_{\perp}(\omega)$ and $\chi''_{\perp}(\omega)$ for values of $0.5 < Kv/kT < \infty$. In the experimental studies presented here, a system was used in which Kv/kT had values in the range 1–5, reflecting the particle-size distribution. However, the application of a polarizing magnetic field H to the sample effectively results in an increase in the barrier Kv (and hence an increase in Kv/kT) which the magnetic moments must overcome. This increase in H results in less spontaneous flipping of the magnetic moments (Néel relaxation) and increasing dominance to $\chi(\omega)$ from resonance. The effect is also to shift $f_{\rm max}$ from 1.0 to 4.7 GHz and $f_{\rm res}$ from 1.65 to 5.0 GHz. The result of this is that the value of $f_{\rm max}$ corresponding to the maximum in the value of $\chi''(\omega)$ (loss-peak) approaches the value of $f_{\rm res}$ as resonance becomes the dominant process, as found experimentally (figure 3) and as predicted by Raikher and Shliomis [3].

The corresponding normalized after-effect functions, $b(t)/b(0)$, were determined for 17 values of polarizing field, and are shown in figure 4. These plots clearly demonstrate that with increasing polarizing field $b(t)/b(0)$ gradually becomes oscillatory in nature with an approximate time-constant time of 0.7×10^{-10} s being obtained for maximum H (curve 17), as compared to a time of 3.4×10^{-10} s (curve 1) obtained for the unpolarized case. Thus there is an approximate fivefold increase in the rate of decay of $b(t)/b(0)$ over the range of polarizing field. This rapid increase in the decay process arises because of the effective reduction of the Néel relaxation components ($\tau_{\rm N} = \tau_{\parallel}$) with increasing H, as previously explained. As such, the decaying magnetization corresponds approximately to the transverse susceptibility component, $\chi_{\perp}(\omega)$, and the decay time represents the transverse relaxation time, $\tau_{\perp}(\omega)$, of the particles. This time of 0.7×10^{-10} s corresponds to the time region (10^{-8}–10^{-10} s) normally associated with the prefactor, τ_0, of Brown's equation (13), and is thus a measure of the precessional decay time of the particles magnetic moment.

Furthermore, the periodic time for curve 17 corresponds to a frequency of 4.8 GHz, which is a close approximation to the value of f_{res} obtained from the corresponding $\chi'(\omega)$ curve of figure 1.

4. Conclusion

Measurements of the complex susceptibility, $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$, of a magnetic fluid as a function of the frequency (over the frequency range 50 MHz to 18 GHz) and of the polarizing field (over the range 0–100 kA m^{-1}) have been reported for the first time. Measurements were obtained by means of the short-circuit transmission line technique, with the frequency range being realized by the use of an HP Network Analyser which operates up to 40 GHz. These measurements have resulted in more complete profiles of $\chi'(\omega)$ and $\chi''(\omega)$ than existed previously, with resonance being present for all values of polarizing field. From these profiles, values of resonant frequency, f_{res}, and frequency of maximum absorption, f_{max}, were identified, and the ratio of $f_{\mathrm{max}}/f_{\mathrm{res}}$ as a function of the polarizing field, H, was found to be in accordance with that predicted by Raikher and Shliomis.

A linear relationship was found to exist between f_{res} and H, thereby enabling an average value of the internal anisotropy field, $\overline{H}_{\mathrm{A}}$, and a corresponding average value of the anisotropy constant, $\overline{K}$, to be determined for the sample.

Furthermore, by transformation of the $\chi''(\omega)$ component, the normalized after-effect function, $b(t)/b(0)$, was investigated within a time region of 10^{-11} s with its profile changing from an exponential to an oscillatory form over the polarizing field range, as indicated in figure 4. This effect was attributed to a reduction in the contribution of the relaxational (Néel) components to $\chi(\omega)$ as a result of the polarizing field, and enabled a value of 7×10^{-11} s to be determined for the precessional decay time, τ_0, this value being within the time region normally associated with τ_0.

The measurement system presented here has shown itself to be well suited to the investigation of f_{res} as a function of polarizing field, H, for colloidal suspensions of magnetite particles. It will also be suitable for similar studies on cobalt suspensions which have an unpolarized f_{res} value of approximately 4 GHz [1] and, for the polarizing range used here, an estimated upper f_{res} of approximately 10 GHz. This is something which would not have been possible with the 6 GHz system [1]. Finally, the frequency limit on this work was due to the limitations imposed by the coaxial cell. As the rest of the measurement system can operate at 40 GHz, this is obviously an area for future consideration with a view to doubling the existing measurement frequency range, thereby enabling one to investigate cobalt ferrite particles which have a higher f_{res} value than that of magnetite or cobalt.

Acknowledgments

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