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On the calculation of the Néel relaxation time in uniaxial single-domain ferromagnetic particles

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Abstract. Nanometre-sized particles of ferrite, commonly used in magnetic fluids, are single-domain. The direction of magnetic moment of these small, uniaxial, ferromagnetic particles is known to fluctuate due to thermal agitation, and can relax through the Néel-type relaxation mechanism. The relaxation time of such fluctuations is usually determined by means of Brown's equations for high and low barrier heights. More recently, modified equations catering for a continuous range of barrier heights have been proposed. Comparison of these equations shows that, even in the most extreme case only a factor of approximately 1.7 distinguishes the corresponding eigenvalues (which represent the inverse of the relaxation time). It is concluded that the major source of error in predicting the relaxation time arises, not primarily due to the particular equations used, but because of the large uncertainty in obtaining precise experimental data needed to determine the components, f_0 and σ, of these equations. For example, for a small change in anisotropy constant K by a factor of 2.5 (typical values for the system considered here are $(2–5)\times10^4$ J m^{-3}), the calculated values of Néel relaxation times using Brown's equation differ by a factor of about 37, corresponding to times of 1.6×10^{-7} to 4.3×10^{-9}. An experimental value of 5×10^{-9} s determined from the frequency of the maximum of the loss-peak of the imaginary part of the complex susceptibility is at the outer limit of these calculated values.

1. Introduction

The particles commonly used in magnetic fluids have radii ranging from 2 to 10 nm. As these particles are in the single-domain region, they can be considered to be in a state of uniform magnetization with magnetic moment, m, given by

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

where M_s (Wb m^{-2}) denotes saturation magnetization and v is the volume of the particle. The magnetic moment has preferred orientation(s) (easy axis) relative to the particles due to magnetic anisotropy, K, which generally arises from a combination of shape and magnetocrystalline anisotropy. The magnetic moment may change from one easy direction of magnetization to another by overcoming an energy barrier, which, for uniaxial anisotropy, is given by Kv. This reversal, or switching time, is usually referred to as the Néel relaxation time, τ [1] and Néel, assuming uniaxial anisotropy, estimated the relaxation time τ to be

$$\tau = f_0^{-1} \exp(\sigma) \tag{2}$$

where f_0 is a constant with an often quoted approximate value of 10^9 s^{-1} [2] and σ is the ratio of anisotropy energy to thermal energy (Kv/kT).

2. Brown's equations

Brown [3] realized that Néel's expressions did not take into account the fact that the magnetic moment could spend some time in directions other than at the minimum of the potential well (easy axis). He thus derived a differential equation to describe the motion of the direction of the magnetic moment during its 'random walk' from one energy minimum to another. He did not solve the equation but obtained values for the eigenfunctions, λ_{Br}, for high and low barriers with

$$\lambda_{Br} = 4\pi^{-1/2}\sigma^{3/2}\exp(-\sigma) \qquad \sigma \geqslant 1 \tag{3a}$$

$$\lambda_{Br} = 2\left(1 - \frac{2}{5}\sigma + \frac{48}{875}\sigma^2\right) \qquad \sigma \ll 1. \tag{3b}$$

Now [4],

$$\tau_N = 2f_0^{-1}\sigma/\lambda_{Br} \tag{4}$$

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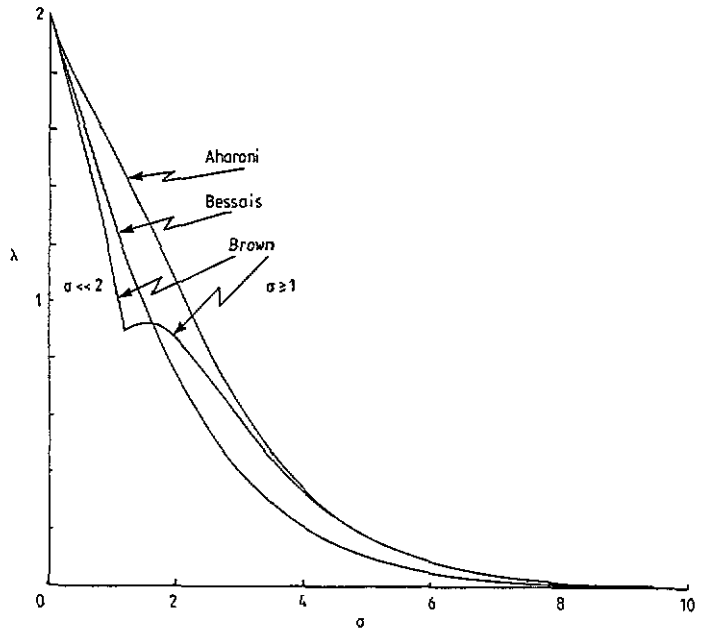

Figure 1. Plot of eigenvalues as determined by Bassais' equation, λ_{Ba}, Aharoni's equation, λ_A and Brown's equation, λ_{Br}, against σ (the ratio of anisotropy energy to thermal energy (Kv/kT)).

where f_0^{-1} is a constant.

Thus from (3*a*)

$$\tau_N = f_0^{-1}\pi^{1/2}\sigma^{-1/2}\exp(\sigma)/2 \qquad \sigma \geqslant 1 \qquad (5)$$

and from (3*b*)

$$\tau_N = f_0^{-1}\sigma\left(1 - \frac{2}{5}\sigma + \frac{48}{875}\sigma^2\right)^{-1} \qquad \sigma \ll 1$$

$$\approx f_0^{-1}\sigma(1 + \tfrac{2}{5}\sigma). \qquad (6)$$

For convenience equations (5) and (6) are generally written in the familiar form

$$\tau_N = \begin{cases} f_0^{-1}\sigma^{-1/2}\exp(\sigma) & \sigma \geqslant 1 \\ f_0^{-1}\sigma & \sigma \ll 1. \end{cases} \qquad (7)$$

An obvious weakness with equations (5) and (6) is that they do not cater for a continuous range of values in the region of $\sigma \approx 1$ and, recognizing this, Bessais *et al* [5] produced, by means of curve fitting, a single empirical expression, namely

$$\lambda_{Ba} = 2(1 + \sigma/4)^{5/2}\exp(-\sigma) \qquad (8)$$

suitable for a continuous range of σ from small to large values of σ. Aharoni [6] further developed this concept of having a single expression and modified equation (8) to arrive at the eigenvalue

$$\lambda_A = 2\left(\frac{1 + 9\sigma/5 + (4/\pi)^{1/3}\sigma^2}{(2+\sigma)}\right)^{3/2}\exp(-\sigma). \qquad (9)$$

which tends to the correct power of $\sigma^{3/2}$ in the limit of $\sigma \ll 1$.

Figure 1 illustrates how the eigenvalues of the respective expressions compare as a function of σ, up to a value of $\sigma = 10$, whilst figure 2 shows that, even in the most extreme case, only a factor of 1.7 distinguishes the different values of λ.

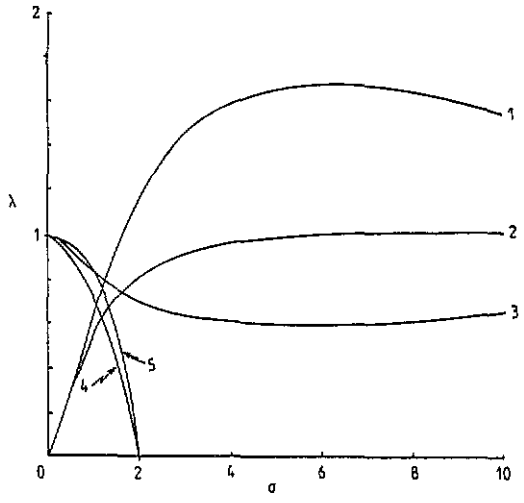

Figure 2. Plot of ratio of eigenvalues as determined by Bessais' equation, λ_{Ba}, Aharoni's equation, λ_A and Brown's equation, λ_{Br}, against σ (the ratio of anisotropy energy to thermal energy (Kv/kT)): 1, $\lambda_{Br}/\lambda_{Ba}$; 2, λ_{Br}/λ_A; 3, λ_{Ba}/λ_A (for $\sigma \geqslant 1$) and 4, $\lambda_{Br}/\lambda_{Ba}$; and 5, λ_{Br}/λ_A (for $\sigma \ll 1$).

The other factor to be taken into account in the determination of τ_N is the pre-exponential component f_0^{-1}, which can be determined from the expression [7]

$$f_0 = [M_s/2\mu_0\gamma\alpha K]^{-1} \qquad (10)$$

where γ is the gyromagnetic ratio and α is a damping constant. An approximate value of α of the order of magnitude of unity [5] has been suggested for the case of small particles whilst values of α have also been variously quoted as being 0.1 or 0.01 [8,9]; a further problem arises in one's choice of α because its

temperature-dependence must be taken into account [5]. Furthermore, the problem of determining τ_N or f_0 from the above equations, in order to make comparisons with experimental values, is compounded by the fact that, for the experimental systems studied, the particles not only have a size distribution but a shape distribution as well. This leads, in turn, to a distribution of values of K, the anisotropy constant. Thus one is immediately confronted with a large uncertainty in the value of σ to be used in these expressions.

As an example, taking M_s to be typically 0.4 Wb m^{-2} for magnetite/maghaemite particles with a median diameter of 11 nm, α as 0.4 and K in the range $(2–5)\times10^4$ J m^3, f_0 has values in the range 4.5×10^9–1×10^{10} s^{-1} and τ_N (using Brown's equations) has values in the range 1.6×10^{-7} to 4.3×10^{-9} s. Literature values for f_0 range from 10^8 to 10^{12} s^{-1} [10, 11]. It is thus perfectly obvious that, in view of the difficulty of obtaining particle systems that can be characterized with sufficient accuracy and confidence, the choice of equation used to determine τ_N is of little significance in situations such as those presented here.

Thus, in view of the difficulty of predicting at what frequency the relaxation should occur, one will perhaps have to rely on a technique that measures it directly.

3. Direct measurement

One effective and proven technique is the toroidal technique of Fannin *et al* [12] whereby, as a result of swept measurements taken over a wide frequency range, the real and imaginary components of the complex AC magnetic susceptibility of a ferrofluid, $\chi'(\omega)$ and $\chi''(\omega)$ respectively, are obtained.

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

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega). \tag{11}$$

According to Debye's theory [13] the complex susceptibility, $\chi(\omega)$, has a frequency-dependence given by the approximate equation

$$\chi(\omega) = \chi_0/(1 + i\omega\tau_N) \tag{12}$$

$$= \chi_0/(1 + \omega^2\tau_N^2) - i\omega\tau_{eff}\chi_0/(1 + \omega^2\tau_N^2) \tag{13}$$

with

$$\chi_0 = nm^2/3kT\mu_0 \tag{14}$$

where n is the particle number density.

Equation (13) demonstrates how $\chi'(\omega)$ falls monotonically whilst the $\chi''(\omega)$ component has a maximum given by

$$\omega_{max}\tau_N = 1. \tag{15}$$

Therein lies the relationship with λ, for as has previously been stated, the relaxation time is inversely proportional to λ, which means that ω_{max} is directly proportional to λ. So from a plot of λ versus σ we can, by inspection, determine the effect each of the respective eigenvalues have on the position of the loss-peak and, from the example given, the maximum error in the position of ω_{max} will be 1.7.

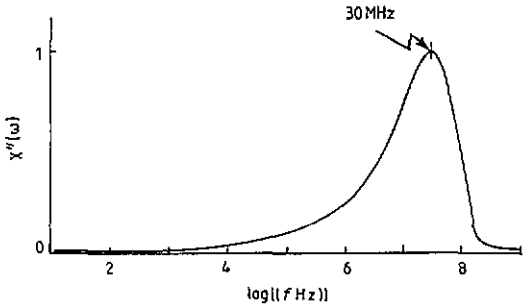

Figure 3. Normalized plot of the imaginary component of the complex susceptibility $\chi''(\omega)$ against log(f Hz) for ferrofluid suspension of magnetite/maghaemite particles with a median diameter of 11 nm.

A typical result obtained using the method of Fannin *et al* for a distribution of magnetite particles in a solid matrix is shown in figure 3. This is a plot of $\chi''(\omega)$ versus log(f Hz) over the frequency range 10 Hz to 1 GHz. The particles in this sample have a median diameter of 11 nm for a log-normal volume distribution, a σ of 5.9 ± 2.5 and a M_s of 0.4 Wb m^{-2}. The loss-peak has a maximum at a frequency of 30 MHz, which, from equation (15), results in a relaxation time of 5.3×10^{-9} s, which is roughly at the outer limit of the range of values calculated using Brown's equations in the example given in section 2.

4. Conclusion

Brown's equations for calculation of the Néel relaxation time, τ_N, have been compared with recently reported modified versions and it has been shown that, at a maximum, the calculated values of relaxation time differ by only a factor of approximately 1.7. However, the possibility of a far greater error exists because of the uncertainty in determining values for the components, f_0 and σ, of these equations.

For a typical magnetic fluid containing ferrite particles of 11 nm median diameter the calculated value of Néel relaxation time using Brown's equations has a wide spread of values, 1.6×10^{-7} to 4.3×10^{-9} s for a small range in values of anisotropy constant $K(2–5) \times 10^4$ J m^{-3}, typically quoted for such systems. An experimental value of 5×10^{-9} s was determined from the maximum of the loss-peak of the imaginary component of the complex susceptibility, which is at the outer limit of the calculated values.

It is concluded that, in view of the difficulty of obtaining particle systems that can be characterized with sufficient accuracy and confidence, the choice of equation used to determine τ_N, where the eigenvalues differ by no more than a factor of 1.7, is of little significance. Thus, in this context, there is little to be gained by the exercise of modifying Brown's equations.

Acknowledgment

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