Effect of a Magnetic Field on the Superparamagnetic Relaxation Time

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The relaxation time for the fluctuations in the direction of the magnetization vector is calculated for very fine, single-domain ferromagnetic particles which have a uniaxial (shape or crystalline) anisotropy. A magnetic field is assumed to be applied parallel to the easy magnetization axis, and the relaxation time is computed for various magnitudes of this field. It is found that the commonly used approximation for high-energy barriers is about as justified as in the case of zero magnetic field, down to barriers of the order of kT.

I. INTRODUCTION

IN very small particles of ferromagnetic materials, thermal agitation causes changes in the orientation of the magnetization of each particle. An assembly of such particles then reaches a statistical distribution of the orientations and behaves as if it was made of paramagnetic atoms. Therefore the phenomenon is called "superparamagnetism."[1] Obviously, this phenomenon can be observed in extremely fine particles only, because for larger particles the relaxation time associated with the thermal agitation is very large, so that the magnetic moments of the particles do not change appreciably during the time of the experiment, and these changes can be ignored.

The usual theoretical study of the relaxation time of this thermal agitation[1] is based on the assumption that the energy barrier between energy minima is so large, compared with kT, that it justifies a discrete-orientation model. Thus, one considers essentially the probability of populating the energy minima, not allowing the magnetization vector any directions in between. This leads to a relaxation time τ which is usually written as[1]

$$1/\tau = f_0 e^{-E_B/kT}, \tag{1}$$

where E_B is the barrier energy, k is Boltzmann's constant, T is the temperature, and f_0 is usually set equal to some quantity having the dimension of frequency—for example, the natural frequency of gyromagnetic precession. Such a simplified model should break down where the minima are rather flat, as has been argued by Brown,[2] yet this model is still the only one used for analyzing experimental data.

Brown[2] has shown that the problem is not that of a correlation time, but rather the response time of the magnetic moments to random forces. He could, therefore, use the theory of stochastic processes and write a Fokker–Planck-type differential equation. For the particular case when the energy density of each particle F is a function of the polar angle θ only, and is independent of ϕ, this equation is[2]

$$(d/dx)[(1-x^2)e^{-F\beta}(d\Phi/dx)] + \lambda e^{-\beta F}\Phi = 0. \tag{2}$$

Here Φ is proportional to the probability-density distribution function, and

$$x = \cos\theta, \quad \beta = V/kT, \tag{3}$$

where V is the volume of the particle. The eigenvalues λ are determined by the requirement that Φ should be regular at $x = \pm 1$, and are related to the relaxation time τ of the system by

$$\lambda = (V/kT\tau\eta)(\gamma_0^{-2} + \eta^2 M_s^2), \tag{4}$$

where M_s is the saturation magnetization and γ_0 is the gyromagnetic ratio. The dissipation constant η can be taken[3] as the value which minimizes λ of (4),

$$\eta \simeq \gamma_0^{-1} M_s^{-1}. \tag{5}$$

Substituting in (4),

$$\lambda = (2VM_s/kT\tau\gamma_0). \tag{6}$$

For practical purposes it is sufficient to calculate the *smallest* nonvanishing eigenvalue λ, because the larger eigenvalues have very little effect on the physical behavior of the system, except at the very early stages of an approach to equilibrium.[2]

The eigenvalue of Eq. (2) has been calculated[4] only for the case of uniaxial anisotropy, in zero magnetic field. This calculation will be extended here, for the case of a magnetic field applied along the easy axis of the uniaxial anisotropy.

II. THEORY

When the magnetization is at an angle θ to the easy axis of a uniaxial anisotropy, along which a field $\mathbf{H}$ is applied, the energy density of the particle is

$$F = -HM_s \cos\theta + K \sin^2\theta. \tag{7}$$

Using (3), and substituting into (2),

$$(1-x^2)d^2\Phi/dx^2 + 2[\alpha(x+h)(1-x^2) - x]d\Phi/dx + \lambda\Phi = 0, \tag{8}$$

where

$$\alpha = KV/kT, \quad h = HM_s/2K. \tag{9}$$

[1] I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), pp. 271–294.

[2] W. F. Brown, Jr., Phys. Rev. **130**, 1677 (1963).

[3] W. F. Brown, Jr., J. Appl. Phys. **30**, 130S (1959).

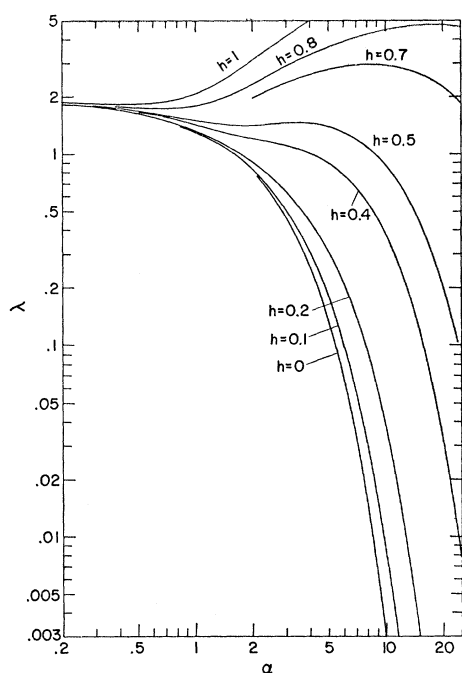[4] A. Aharoni, Phys. Rev. **135**, A447 (1964).

FIG. 1. Eigenvalue λ, which is inversely proportional to the superparamagnetic relaxation time according to Eq. (30), plotted as a function of the reduced energy barrier α and reduced field h, defined in (9), for particles with uniaxial anisotropy K in magnetic field H at temperature T.

In order to solve (8), the solution is expanded in a series of Legendre polynomials,

$$\Phi = \sum_{m=0}^{\infty} a_m P_m(x). \tag{10}$$

Substituting in (8), and using the differentiating and recurrence formulas[5] of the Legendre polynomials, it is seen that (10) is a solution of (8) provided for every $m \geq 0$,

$$\frac{(m+1)(m+2)(m+3)}{(2m+3)(2m+5)} a_{m+2} + \frac{(m+1)(m+2)}{2m+3} h a_{m+1}$$

$$+ \left(\frac{\lambda - m(m+1)}{2\alpha} + \frac{m(m+1)}{(2m-1)(2m+3)} \right) a_m$$

$$- h \frac{m(m-1)}{2m-1} a_{m-1} - \frac{m(m-1)(m-2)}{(2m-1)(2m-3)} a_{m-2} = 0. \tag{11}$$

For the case $h=0$, the even and odd terms were separated,[4] which is also clear from (11), and the three-term recursion formula could be replaced by a continued fraction, from which the eigenvalue could be readily computed. This method is not practical with

[5] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand, Inc., Princeton, N. J., 1956), 2nd ed., p. 106.

a five-term recursion formula (11), and the following procedure was used. The determinant of the coefficients of a_m in (11) should vanish so that (11) will have a nonvanishing solution for the a_m's. The determinant of the coefficients of a_m, up to a certain order n, was therefore equated to zero, and the smallest nonvanishing root λ was computed. Then n was increased, and the smallest root was computed again, until the increase in n had a negligible effect on the eigenvalue.

It should be noted that (11) has the trivial solution $a_m = 0$ for every $m \neq 0$, with $\lambda = 0$. This is the equilibrium solution[2] that is of no interest. However, it can be readily eliminated from the numerical computations by removing the equation with $m = 0$ from (11), since this is the only equation in which a_0 appears.

For each order n of the determinant (and for given h and α), two methods were tried for computing the roots: the Newton-Raphson method[6] and the iteration method[6] in which the eigenvalue is replaced by its previous approximation in every place along the diagonal, except for the first place, which is used to compute the next approximation. Both methods were found to converge after a few iterations, for every order of the determinant. The main difficulty was the necessity of increasing the order of these determinants with increasing α, especially for the larger h, until an order of 30 to 40 had to be used. This became time consuming even for the fast computer.

The computations were carried out on the Golem, the electronic computer of this Institute. Special care was taken to make sure the iteration converged into the *smallest* zero of the determinant. This was checked by using the two iteration processes, and by usually starting at too small a value. Also, for several values of h and α, the determinant was computed for many
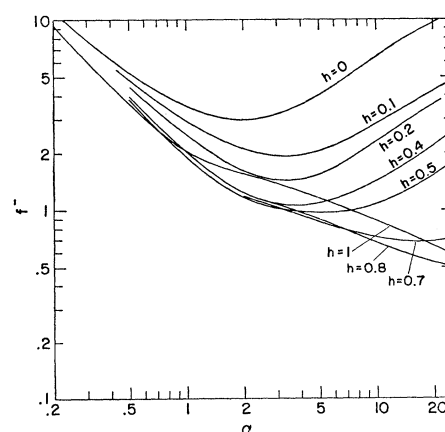

FIG. 2. Parameter f^-, defined in Eq. (13b), calculated from the data of Fig. 1 and plotted as a function of the reduced energy barrier α and the reduced field h. The commonly used approximation (1), with a constant f_0, is equivalent to the assumption that f^- is a constant.

[6] Reference 5, pp. 492–493 and p. 503.

values of λ between zero and the computed eigenvalue, to see that the determinant did not change its sign in between.

The results of the computations are plotted in Fig. 1, for α varying between 0.2 and 25, which is the value usually used[1] as the onset of superparamagnetism, by assuming Eq. (1) and a "measurement time" of 10^2 sec. For values of α smaller than those plotted in Fig. 1, the low-energy-barrier-approximation formula of Brown[2] should hold. Values of h start at $h=0$, which has already been computed before,[4] and increase up to $h=1$, which is the value[2] at which the two-minima structure of (7) disappears.

It should be particularly noted that the determinant contains only even powers of h, so that Fig. 1 is the same when h is replaced by $-h$.

III. RESULTS

The energy (7) has two minima, separated by a maximum. It is readily seen by differentiating (7) that the energy difference between the maximum and each of the minima is

$$E_B = KV(1 \pm h)^2. \tag{12}$$

Therefore, if (1) is to be used, the "constant" f_0 is, according to (6) and (9),

$$f_0 = \gamma_0(K/2M_s)f^{\pm}, \tag{13a}$$

where

$$f^{\pm} = (\lambda/\alpha) \exp[\alpha(1 \pm h)^2]. \tag{13b}$$

The dependence on the volume of the particle and on the temperature of f_0 is in the α dependence of f^+ or
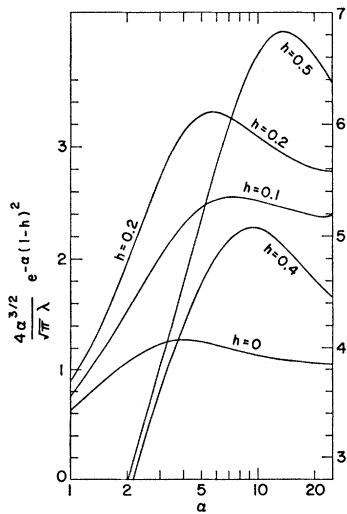
FIG. 3. Ratio of the approximation (14) to the actual eigenvalue of Fig. 1, plotted as a function of the two parameters of Fig. 1. In regions where the expression plotted can be approximated by 1, Eq. (14) can be used. For $h=0.4$ and $h=0.5$, use shifted scale on the right-hand side.
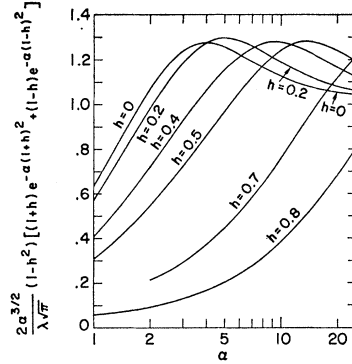
FIG. 4. Ratio of Brown's asymptotic solution (15) to the exact eigenvalue of Fig. 1, plotted as a function of the two parameters of Fig. 1. The curve for $h=0.1$ was also computed, but it was not plotted because it is too close to $h=0$.

f^-. Now, f^+ depends very strongly on α. The dependence of f^- on α, as computed from the data of Fig. 1, is plotted in Fig. 2. It is seen that the variation of f^- is rather slow, so that its replacement by a constant (as is usually done) is a reasonably good approximation, if one is interested only in the order of magnitude of the relaxation time.

A considerably better approximation can be obtained by taking f^- proportional to $\alpha^{1/2}$, that is, by using in (1)

$$f_0 \simeq \gamma_0 K\alpha^{1/2}/M_s. \tag{14}$$

This is more or less in accordance with the asymptotic solution[2] for large α, if h is small. For $h=0$, the data of Fig. 2 yield a constant to within about 10%, for f_0 of Eq. (14) when α changes between 2 and 25. For other values of h, it is seen from Fig. 2 that f^- becomes proportional to $\alpha^{1/2}$ [which makes f_0 of (14) a constant], for the larger values of α. Therefore, the use of (14), rather than just a constant for f_0, should improve the approximation, at least for the smaller values of h. For $h \geq 0.5$, the use of (14) becomes impractical. This is illustrated in Fig. 3, which essentially plots $\alpha^{1/2}/f^-$ (the factor $2\pi^{-1/2}$ was introduced because it appears in the asymptotic solution,[2] but can certainly be taken as 1 for all practical purposes). Equations (14) and (1) yield a good approximation to the relaxation time, as long as the quantity plotted in Fig. 3 can be approximated by 1; and it is seen from the figure that this is the case for h not too large, and α not too small. One might even introduce an h-dependent factor into (14) and thus improve the approximation.

Actually, the asymptotic formula of Brown[2] for the case of energy given by (7) is

$$\lambda = 2\pi^{-1/2}\alpha^{3/2}(1-h^2)\{(1+h) \exp[-\alpha(1+h)^2]$$
$$+ (1-h) \exp[-\alpha(1-h)^2]\}. \tag{15}$$

It has been noted before[7] that the first exponential can

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[7] E. Kneller and E. P. Wohlfarth, J. Appl. Phys. **37**, 4816 (1966).

be omitted, for small h. For larger h, the use of (15) should yield a considerably better approximation than the use of (14). This can be seen from Fig. 4, in which the ratio between the λ of (15), and the actual eigenvalue λ, from Fig. 1, is plotted as a function of α with h as a parameter. The constancy is considerably better than in Fig. 3, but not sufficiently so to justify the complications involved in using (15), for present day experimental accuracy.

IV. DISCUSSION

From the foregoing one can conclude that for the region $h \lesssim 0.4$ and $\alpha \gtrsim 2$, the relaxation time can be approximated by (1) and (14), in which α is defined in (9), K is the anisotropy, M_s is the saturation magnetization, and γ_0 is the gyromagnetic ratio, of the material under study. In principle it should be possible to verify experimentally if this approximation is better than the cruder one of assuming f_0 to be a constant. This can be done by a series of measurements, in which the transition from ferromagnetic to superparamagnetic behavior is found for various values of α, by changing either the volume or the temperature.

Generally speaking, there are two independent methods[8] for measuring the critical α for which there is a transition from ferromagnetism to superparamagnetism (i.e., for which the relaxation time becomes equal to the time of the experiment). In the first method, measurement of an appropriate property of the material are carried out at a constant temperature "for a series of samples with known average particle sizes which encompass the transition region between superparamagnetic and ferromagnetic behavior."[8] From these one can find out the volume in which the transition occurs. However, in order to compare to (14), such a measurement should be repeated at several temperatures, whereas measurements reported so far[8,9] were confined to one temperature.

In the second method, one sample is measured at different temperatures. For an appropriately chosen sample, the transition temperature is within the region of temperatures measured, and can be found from these measurements. Again, measurements were reported[8,9] for one sample, whereas several samples, with different average volume, have to be studied in order to check (14). Moreover, comparing the results of the two methods does not yield any additional information, because in the reported experiments[8,9] the temperature chosen for measurements in the first method is very near to the critical temperature of the second method.

It should be particularly noted that for any accurate determination of f_0, one has to know KV accurately. This is rather difficult because there is always a distribution of V, which is not necessarily the same in different samples of the same material. Also, there can be a distribution in K, if it contains a contribution from shape anisotropy,[10] since the shape varies considerably from particle to particle, and especially since one very often[11] encounters a tendency of the particles to form long chains which have a high shape anisotropy.

Finally, it seems adequate to emphasize that the calculations reported here are for uniaxial anisotropy only. The result does not necessarily apply to materials with cubic anisotropy, for which some measurements[12] have recently been reported. However, because the approximation (14) is essentially that of the asymptotic solution, without even taking the field into account properly, it seems very likely that the same approximation should hold for cubic anisotropy as well.

ACKNOWLEDGMENT

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