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Thermal Agitation of Single Domain Particles

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The direction of magnetization of fine single-domain particles is known to fluctuate because of thermal agitation. The relaxation time for these fluctuations is calculated here for the case of uniaxial anisotropy and zero magnetic field. It is found that the commonly used approximation for high-energy barrier is still a good approximation when the barrier is of the order of kT. For lower barriers, the eigenvalue is expressed as a power series in the energy barrier in terms of kT.

1. INTRODUCTION

EXTREMELY fine particles of ferromagnetic materials have no hysteresis, and generally behave as if each particle was a paramagnetic atom.[1] It is believed that this phenomenon, which is known as "superparamagnetism," is due to thermal agitation which causes continual changes in the orientation of the magnetic moment of each particle, yielding a statistical distribution of orientations. For larger particles, the relaxation time associated with these fluctuations becomes so large that the moments are stable within the measurement time and the thermal agitation can usually be ignored, except when the system approaches a state of collapse (like a domain nucleation), in which case the thermal agitation might help to overcome the energy barrier and cause nucleation[2] slightly below the field which would have made it possible from static equilibrium considerations. In the intermediate size range, between superparamagnetism and stable ferromagnetism, a "magnetic viscosity" is observed, namely the magnetization changes lag behind field changes.[3] This intermediate size range is rather narrow, and for a fixed time of measurement there is a rather sharp change of magnetic properties when the particle size is changed.[4]

In the theoretical study of the relaxation time associated with the thermal fluctuations, it has usually been assumed[1,3,5] that the energy barrier between stable states is so large, compared with kT, that the directions of magnetic moments of the particles are concentrated at the energy minima. One obtains then that the relaxation time is essentially proportional to $\exp(E_B/kT)$, where E_B is the barrier energy, and T is the temperature. This approach is certainly valid only for high-energy barriers, but no quantitative estimation has ever been made for the range of its validity. Stacey[6] has obtained a similar expression using noise theory, only he ignored the possible time lag between application of random forces and the response to them by the system under study. More recently, Brown[7] treated the problem using the theory of Brownian motion. He obtained the relaxation time as eigenvalue of a certain differential equation, which should hold true for high- as well as for low-energy barriers. Unfortunately, however, Brown did not calculate the actual eigenvalues of his equation. He obtained a formula similar to the one which is usually used, as a limiting value for high-energy barriers, and calculated up to a second order in the energy, the values for low-energy barriers. Therefore, he could not give any reliable estimation for the range of validity of the commonly used high-energy-barrier approximation.

It is the purpose of the present paper to calculate the actual eigenvalue of Brown's equation as a function of the energy barrier. It will be shown that the high-energy-barrier approximation can be safely used down to barriers of the order of kT, and power-series expansion will be given for lower barriers. We shall be specifically interested in the physically most interesting case of a uniaxial anisotropy energy (which can be either shape or magnetocrystalline anisotropy), namely, when the energy density of each particle is

$$F=K\sin^2\theta. \tag{1}$$

Here K is the anisotropy constant, and θ is the angle between the magnetization direction and the particle's easy axis. It is further assumed that there is no external field. Introducing the notations

$$x=\cos\theta,\quad \alpha=KV/kT, \tag{2}$$

where V is the volume of the particle, Brown's eigenvalue equation[7] for this particular case becomes

$$\frac{d}{dx}\left[(1-x^2)\frac{d\Phi}{dx}\right]+2\alpha x(1-x^2)\frac{d\Phi}{dx}+\lambda\Phi=0. \tag{3}$$

Here Φ is proportional to the probability density distribution function, and the eigenvalue λ is related to the relaxation time τ of the system into stable equilibrium

[1] C. P. Bean and J. D. Livingston, J. Appl. Phys. Suppl. **30**, 120S (1959).
[2] A. Aharoni, J. Appl. Phys. **33**, 1324 (1962). See also A. Aharoni and E. Neeman Phys. Letters **6**, 241 (1963); A. Aharoni, Rev. Mod. Phys. **34**, 227 (1962).
[3] L. Néel, Ann. Geophys. **5**, 99 (1949).
[4] E. F. Kneller and F. E. Luborsky, J. Appl. Phys. **34**, 656 (1963).
[5] W. F. Brown, Jr., J. Appl. Phys. Suppl. **30**, 130S (1959).
[6] F. D. Stacey, Proc. Phys. Soc. (London) **73**, 136 (1959).
[7] W. F. Brown, Jr., Phys. Rev. **130**, 1677 (1963); See also W. F. Brown, Jr., J. Appl. Phys. **34**, 1319 (1963).

by:

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

where M_s is the saturation magnetization, γ_0 is the gyromagnetic ratio, and η is a dissipation constant. The latter can be found from experimental linewidths and can be usually taken[5] as

$$\eta\simeq\gamma_0^{-1}M_s^{-1}, \quad (5)$$

which is the value of η that minimizes λ, according to (4).

Equation (3) has to be solved with the boundary condition that Φ is regular at $x=\pm1$. This should lead to discrete eigenvalues, λ_n. The lowest of these is $\lambda=0$, associated with the eigenfunction $\Phi=$const, which describes a steady state. The method to be described in the following section can be used to calculate any of the other eigenvalues λ_n, as functions of the reduced energy barrier, α. However, it will be specifically applied to the smallest positive eigenvalue λ_1 which is of most physical interest.

2. THE EIGENVALUE λ_1

When α vanishes, Eq. (3) reduces to the differential equation of Legendre polynomials. Therefore,

$$\lambda_n(0)=n(n+1),$$

and in particular

$$\lambda_1(0)=2.$$

This suggests expanding Φ in a series of form

$$\Phi=\sum_{m=0}^{\infty} a_m P_m(x), \quad (6)$$

where P_m are the Legendre polynomials. Substitution of (6) in (3), with the subsequent use of the Legendre differential equation, differentiation and recurrence formulas,[8] yield the following 3-term recursion formula for the coefficients a_m:

$$\frac{(m+1)(m+2)(m+3)}{(2m+3)(2m+5)}a_{m+2}+\left(\frac{\lambda-m(m+1)}{2\alpha}+\frac{m(m+1)}{(2m-1)(2m+3)}\right)a_m-\frac{m(m-1)(m-2)}{(2m-1)(2m-3)}a_{m-2}=0, \quad (m\geqslant 0). \quad (7)$$

It is seen that as $m\to\infty$, either $a_m/a_{m-2}\simeq 2m/\alpha$ or $a_m/a_{m-2}\simeq-\alpha/2m$. Of these two solutions for the second-order difference equation (7), the former obviously represents a diverging series when substituted in (6). The latter represents a series that converges like $\exp(-\frac{1}{2}\alpha)$ uniformly in x, and is thus the solution that fulfills the boundary conditions. It is also readily seen from (7) that there is no interaction between terms with odd values of m, and those with even values. The odd and even functions Φ can thus be treated separately. The eigenvalue of most interest λ_1 belongs to the odd-functions set.

Let the following notations be introduced for brevity:

$$N_m=\frac{2\alpha m(m+1)}{(2m-1)(2m+1)}\frac{a_m}{a_{m-2}}, \quad (m\geqslant 2) \quad (8)$$

$$\beta_m=\frac{4\alpha^2m^2(m-1)(m-2)}{(2m-3)(2m-1)^2(2m+1)},$$

$$\gamma_m=m\left[1-\frac{2\alpha}{(2m-1)(2m+3)}\right], \quad (m\geqslant 0). \quad (9)$$

Substituting these relations in (7) and rearranging, one obtains

$$N_m=\beta_m\{[\lambda/(m+1)]-\gamma_m+N_{m+2}\}^{-1}, \quad (m\geqslant 2) \quad (10)$$

and

$$N_2=-\lambda, \quad N_3=1-(\tfrac{1}{2}\lambda)-(\tfrac{2}{5}\alpha). \quad (11)$$

As was mentioned before, a_m/a_{m-2} tends to zero as $-\alpha/2m$ when $m\to\infty$ and therefore $N_m\to 0$ as $\alpha^2/4m$. This ensures convergence of the infinite continued fraction obtained by iterating Eq. (10):

$$N_m=\cfrac{\beta_m}{[\lambda/(m+1)]+\gamma_m+\cfrac{\beta_{m+2}}{[\lambda/(m+3)]+\gamma_{m+1}+\cfrac{\beta_{m+4}}{[\lambda/(m+5)]+\gamma_{m+2}+\cdots}}}. \quad (12)$$

One can in principle start with any m, and obtain the left-hand side of (12) by working the recurrence relation (10) upwards, to one of the values given by (11). Using (9), Eq. (12) is then a transcendental equation, which can be solved[9] for λ as a function of α, and one

[8] E. Jahnke and F. Emde, *Tables of Functions With Formulas and Curves* (Dover Publication, New York, 1945), 4th ed., pp. 114, 115.

[9] Details are essentially as in the calculation of the eigenvalues of spheroidal wave functions. See Carson Flammer, *Spheroidal Wave Functions* (Stanford University Press, Stanford, California, 1957), Chap. 3.

can obtain all the eigenvalues by starting with different values of m in (12). In particular, it is readily seen that the first nonzero eigenvalue λ_1 is obtained for $m=3$. For this case one obtains from (12)

$$1-(\tfrac{1}{2}\lambda)-(\tfrac{2}{5}\alpha)=O(\alpha^2),$$

or

$$\lambda_1=2-(\tfrac{4}{5}\alpha)+O(\alpha^2).$$

Substituting in (12), and going one term further:

$$1-\frac{\lambda}{2}-\frac{2\alpha}{5}=-\frac{48\alpha^2}{875[1+(2\alpha/75)+0(\alpha^2)]},$$

and by using the binomial theorem one can obtain from this relation the terms α^2 and α^3 in λ_1, etc. Using this procedure,[9] one obtains

$$\lambda_1=2\sum_{n=0}^{\infty}c_n(\tfrac{2}{5}\alpha)^n, \tag{13}$$

with:

$c_0=+1$ $\quad c_4=-0.01030480$

$c_1=-1$ $\quad c_5=+0.00081434$

$c_2=+0.34285714$ $\quad c_6=+0.00022854$

$c_3=-0.02285714$ $\quad c_7\simeq 5\times10^{-5}$.

The terms c_1 and c_2 were calculated by Brown[7] using second-order perturbation theory. The terms added here are sufficient to compute λ_1 with an accuracy of better than 1% for moderate values of α, up to about 4. For larger values of α, the eigenvalue λ_1 was computed directly[9] from the transcendental equation (12). The results are plotted in Fig. 1, curve (a).

For large values of α, Brown[7] gave the asympototic formula

$$\lambda_1=4\pi^{-1/2}\alpha^{3/2}e^{-\alpha}. \tag{14}$$

This function is plotted in Fig. 1, curve (b). It is seen that already in the region shown, this approximation is good enough, so that there is no point in continuing the exact computations any further.

3. DISCUSSION

The high-energy-barrier approximation, Eq. (14), which was derived by Brown[7] using the assumption $\alpha\gg1$, turns out to be a good approximation even when α almost equals 1, i.e., when the energy barrier is about kT. Especially if one is interested just in the order of magnitude of λ, as is often the case, one can actually use this approximation for all practical cases studied so far. For standard experimental techniques involving measurements of magnetic properties, the time of measurement can be taken[1] as 10^2 sec, in which case one can study with reasonable accuracy only properties of particles for which α is not much smaller than the "critical" value[1,4] of about 25. Although experimental points are given by Kneller and Luborsky,[4] for example, for $D/D_p=0.4$, which corresponds to $\alpha=1.6$, what one actually measures for such values of α is evidently the size distribution of particles. Even with Mossbauer effect, in which the "time of measurement" can be taken as 10^{-8} sec, one can hardly approach the region of α where there is any appreciable difference between the two curves in Fig. 1, unless something is done about the size distribution of the particles. It is probably only with detailed experiments of the type mentioned by Roth,[10] namely, studying magnetic scattering of neutrons for which the passage time through the particle is of the order of 10^{-13} sec, that one might be able to distinguish experimentally between the two curves of Fig. 1.

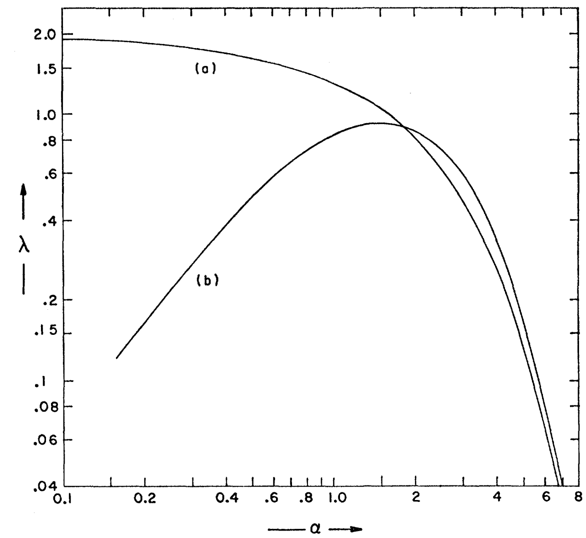

FIG. 1. The first positive eigenvalue λ of Brown's equation (3), which is inversely proportional to the product of the absolute temperature and the relaxation time τ according to (4), plotted as a function of the reduced energy barrier $\alpha-KV/kT$. Curve (a): The actual eigenvalue. Curve (b): Brown's approximation for $\alpha\gg1$, Eq. (14).

For α less than about 1.5 the high-energy-barrier approximation starts a rather fast decrease, while the correct eigenvalue continues to increase slowly. In this region, the correct eigenvalue can be computed to a very high accuracy from the series (13).

It should be finally noted that the transcendental equation (12) yields the higher eigenvalues λ_n, besides the first one λ_1 discussed here. If they are of any interest, these eigenvalues can be computed directly from (12), or by constructing a series similar to (13).

[10] W. L. Roth, Acta Cryst. 13, 140 (1960).