Distribution of Fields from Randomly Placed Dipoles: Free-Precession Signal Decay as Result of Magnetic Grains

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Free-precession signals were observed from fluids in samples containing randomly distributed ferromagnetic grains. The local free-precession phase shift was calculated by computing volumes of space for various ranges of perturbing field strength near individual grains. The frequency of occurrence of a given phase shift caused by individual grains is inversely proportional to the square of the phase shift, this distribution being a limiting case of the Cauchy form. The resultant distribution of phase shifts from effects of many grains is then still of the Cauchy form. This leads to an exponential signal decay, with the rate independent of diffusion. If M is the algebraic sum of the individual dipole moments of the individual magnetic grains per unit volume, and γ the magnetogryic ratio, $1/T_2=(8\pi^2/9\sqrt{3})M\gamma$ if all grains are magnetized parallel to the precession field; $1/T_2=(4\pi/3)M\gamma$ if perpendicular. Within 10%, $1/T_2=4.6M\gamma$ for any random or systematic orientation of the grains. Measurements on water containing magnetite powder stabilized by carboxymethylcellulose and on glycerine containing magnetite powder, as well as on sands containing magnetite powder and saturated with water or glycerine, verified the exponential decay, independence of decay rate on diffusion or viscosity, and the above numerical value of decay rate (with small geometrical correction applied to results for the sand system).

INTRODUCTION

FOR various reasons nuclear magnetic resonance (NMR) measurements have been made on fluids in porous solids or fluids containing suspended solids. It has long been known that both transverse and longitudinal relaxation times for protons in fluids in these systems are reduced by interaction with the solid.[1–6] Paramagnetic powders have been used for the purpose of reducing relaxation times,[1] and relaxation time measurements have been made to determine fluid accessibility to paramagnetic catalyst surfaces.[2,3] Relaxation times for fluids in contact with surfaces of solids nominally free of para- or ferromagnetic materials give information concerning the adsorption of the fluid on the surfaces.[3–5] In some measurements, an objective may be to obtain proton precession signals from a fluid in a porous material as an indication of the amount of fluid,[7] where para- or ferromagnetic materials may merely interfere with the measurements.

Most natural rocks have some ferromagnetic inclusions, and so do many artificial porous or granular materials such as glass beads or alumina sand. Even in some very clean quartz and limestone, permanent magnetization could be demonstrated.

Nuclear magnetism measurements are now used in the logging of oil wells, where a proton precession instrument is run in a borehole to obtain signals from oil and water in the pores of the surrounding rock.[7] Here, ferromagnetic minerals in the rock usually shorten signal decay times considerably by means of the locally inhomogeneous fields produced. On the other hand, it is advantageous to introduce ferromagnetic particles into the fluid within the borehole in order to provide so rapid a signal decay that signals from this fluid are not observed.

Because of the occurrence of ferromagnetic materials in the many samples mentioned, it is desirable to know the effect of the magnetic particles on free-precession signal decay or the corresponding effect on NMR line shape. As will be shown for a large range of conditions, the signal decay is exponential and does not depend on the temperature or diffusion rate of the fluid.

A previous calculation[8] for a crystal containing randomly distributed paramagnetic centers showed that the NMR line shape is approximately Lorentzian if only a small fraction of the sites are paramagnetic. This is a different problem from the present one in that the magnetic sites are limited to crystal lattice points and in that the problem is an essentially quantum mechanical one.

THEORETICAL

Definition of the System—Assumptions and Approximations

The free-precession signal decay envelope will be calculated for a fluid containing magnetic particles dispersed in it. The following assumptions and simplifications are made:

(a) The fluid sample contains a large number of fixed macroscopic magnetic grains (dipoles), which need not be all of the same strength.

(b) The sample is large enough that the region of significant influence of most of the grains is within the sample.

[1] W. G. Proctor and F. C. Wu, Phys. Rev. **78**, 471 (1950); F. Bloch, Phys. Rev. **83**, 1062 (1951).
[2] P. W. Selwood and F. K. Schroyer, Discussions Faraday Soc. **8**, 337 (1950).
[3] T. W. Hickmott and P. W. Selwood, J. Phys. Chem. **60**, 452 (1956).
[4] R. J. S. Brown and I. Fatt, Petrol. Trans. Am. Inst. Mining Met. Engrs. **207**, 262 (1956); R. J. S. Brown, Bull. Am. Phys. Soc. **3**, 23 (1958).
[5] J. R. Zimmerman and W. E. Brittin, J. Chem. Phys. **61**, 1328 (1957).
[6] S. Broersma, J. Chem. Phys. **24**, 153 (1956).
[7] R. J. S. Brown and B. W. Gamson, Petrol. Trans. Am. Inst. Mining Met. Engrs. (to be published).
[8] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

(c) Any magnetic grain is as likely to be in any volume element of the sample as in any other volume element of the same size. (As will be seen, the orientation of the grains may be either random or otherwise.)

(d) The magnetic grains are sufficiently compact that they may be considered as point dipoles.

(e) The approximation is made that only the component of the perturbing field parallel to the precession field H_0 is considered.

(f) Neither the magnetic grains nor the signal-giving nuclei move. This assumption will be lifted, however, in the discussion under *Diffusion*.

(g) Relaxation from sources other than the magnetic grains is not considered, and the influence of inhomogeneous fields from other sources is also not considered.

The fulfillment of these assumptions for some real samples will be discussed in a later section.

Distribution of Fields from a Single Dipole

A signal is received from the free precession of nuclei in a precession field $\mathbf{H}_0$. The field $\mathbf{H}_0$ is perturbed by the field from the magnetic grains embedded in the sample. Let H be the component of the perturbing field parallel to $\mathbf{H}_0$. Where the field from the magnetic grain is much weaker than $\mathbf{H}_0$, the resultant field strength determining precession frequency is H_0+H. The free precession signal decay is then determined by the distribution of values of H over the sample. H is the sum of the contributions of the individual magnetic grains. The contribution to H of a single grain is

$$\Delta H=(m/r^3)[(\hat{m}\cdot\hat{H}_0)-3(\hat{m}\cdot\hat{r})(\hat{H}_0\cdot\hat{r})], \tag{1}$$

where m is the dipole moment of an individual grain, a caret indicates a unit vector, and r is the distance from the grain to the precessing nucleus of concern. Let $V(h)$ be the volume of space for which the absolute value of the grain's contribution to H for the given field point is greater than a value h. If $r(h,\vartheta,\varphi)$ is the radius for which $|\Delta H|=h$,

$$V(h)=\tfrac{1}{3}\int_{\vartheta=0}^{\pi}\int_{\varphi=0}^{2\pi} r^3(h,\vartheta,\varphi)\sin\vartheta\,d\vartheta\,d\varphi, \tag{2}$$

$$r^3(h,\vartheta,\varphi)=(m/h)\,|\cos\vartheta_0-3\cos\alpha\cos\vartheta|, \tag{3}$$

where the angles are as defined in Fig. 1.

$$\cos\alpha=\cos\vartheta\cos\vartheta_0+\sin\vartheta\sin\vartheta_0\cos\varphi, \tag{4}$$

$$V(h)=(m/3h)\int_0^{\pi}\int_0^{2\pi}|\cos\vartheta_0\sin\vartheta-3\cos^2\vartheta\cos\vartheta_0\sin\vartheta -3\cos\vartheta\sin^2\vartheta\sin\vartheta_0\cos\varphi|\,d\vartheta\,d\varphi. \tag{5}$$

If we were to omit the absolute value sign in (5), the integral would be zero, indicating that for any orientation of the dipole moment of the grain with respect to the precession field there is as much volume for which the perturbation to the precession field is positive as negative. For the dipole moment of the grain parallel to $\mathbf{H}_0$, or $\vartheta_0=0$,

$$V_{\parallel}(h)=(16\pi/9\sqrt{3})(m/h)\approx 3.22(m/h). \tag{6}$$

If the grain is perpendicular to $\mathbf{H}_0$, or $\vartheta_0=\pi/2$,

$$V_{\perp}(h)=(8/3)(m/h)\approx 2.67(m/h). \tag{7}$$

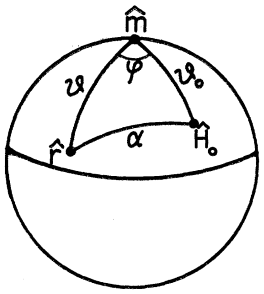

FIG. 1. Relationship among angles used in computation.

Equation (5) is not easily integrated for other values of ϑ_0. However, if one integrates the square of the integrand of (5) instead of the absolute value, the result is seen to be monotonic in ϑ_0, suggesting that values of $V(h)$ for intermediate values of ϑ_0 are intermediate between those given in (6) and (7). The numerical constants in (6) and (7) differ by only 20%, and the dependence on m and h does not vary with ϑ_0, showing that the effect of the dipole is nearly independent of its orientation.

In computing the effect of the dipole field of a magnetic grain on the signal decay envelope, one needs to know at any given time the distribution of phase shifts over the sample. The phase shift due to a field of strength h is $\phi=h\gamma t$, where γ is the nuclear magnetogyric ratio. The volume of space in the vicinity of the magnetic grain for which the phase shift $\geqslant\phi$ for positive ϕ (or $\leqslant\phi$ if ϕ is negative) is $\frac{1}{2}V(h)=\frac{1}{2}V(\phi/\gamma t)$. The element of volume for which the phase shift is between ϕ and $\phi+d\phi$ is

$$dV=(km\gamma t/\phi^2)d\phi, \tag{8}$$

where k is a number between $\frac{4}{3}$ and $8\pi/(9\sqrt{3})$, depending on the orientation of the magnetic grain, as shown in (6) and (7). The probability that some one of the many grains contributing to the perturbing field makes an individual contribution to the phase shift of a given nucleus between ϕ and $\phi+d\phi$ is then $(\sum dV)/(\text{sample vol})$:

$$P(\phi)d\phi=(K/\phi^2)d\phi, \tag{9}$$

$$K=\gamma t(\text{sample volume})^{-1}\textstyle\sum k_i m_i, \tag{10}$$

where the sum is over the contributions of the different grains. If all the magnetic grains are oriented in the same direction,

$$K_{\parallel}=(8\pi/9\sqrt{3})M\gamma t;\quad K_{\perp}=(4/3)M\gamma t, \tag{11}$$

where M is the total dipole moment per unit volume.

Resultant Field from Many Magnetic Grains

The distribution $P(\phi)$ is the limiting case of a Cauchy distribution[9]:

$$P(\phi)=\lim_{\epsilon\to 0}\frac{K}{\phi^2+\epsilon^2}. \tag{12}$$

The phase shift for an element of the sample is the resultant of the contributions from all the individual magnetic grains. Since these grains are independently and randomly placed in the sample, the resultant phase shift at a given point in the sample is the sum of the independent contributions distributed according to the Cauchy distribution. The distribution of these resultants over the sample is then simply another Cauchy distribution.[9] The correlation of contributions to neighboring sample points is neglected, because the sample is large compared to the average spacing between grains; that is, it may be assumed that the phase shifts of all volume elements of the sample are independent.

The distribution of resultant phase shifts for the sample, $W(\phi)$, is then still of the Cauchy form. For large ϕ the chance of having significant contributions from more than one magnetic grain is exceedingly small; so, for large ϕ, $W(\phi)$ must reduce to (9). The remaining parameter in the Cauchy form is easily determined by the required normalization (unit probability that the phase shift for a given volume element of the sample has some value between $-\infty$ and $+\infty$).

$$W(\phi)=K/(\phi^2+\pi^2K^2). \tag{13}$$

The Signal Decay

The signal envelope is then

$$S=S_0\int_{-\infty}^{+\infty}W(\phi)\cos\phi d\phi=S_0e^{-\pi K}. \tag{14}$$

Since K is proportional to t, the signal decay is exponential in time, with transverse relaxation rates

$$(1/T_2)=(8\pi^2/9\sqrt{3})M\gamma, \tag{15}$$

$$(1/T_2)=(4\pi/3)M\gamma, \tag{16}$$

or, in the general case,

$$1/T_2\approx 4.6M\gamma, \tag{17}$$

where M is generalized to represent the algebraic sum of the dipole moments of the individual magnetic grains per unit volume, however oriented. Equation (17) is within 10% of the correct value even for the extreme cases of all grains oriented parallel to or perpendicular to the prceession field.

[9] H. Cramer, *Mathematical Methods of Statistics* (Hugo Grebers, Stockholm, 1946), p. 246.

Diffusion

It was assumed in the above that local fields were constant in time. It might be expected that rapid diffusion would lead to an averaging of local fields with a corresponding reduction of the effect of the inhomogeneous magnetic fields. In the Bloembergen[10] theory of relaxation in liquids, the relaxation is again due to local fields from magnetic dipoles. Here a correlation time for the change of these fields due to molecular motion is defined. The shorter this time, or the more rapid the averaging of local fields, the less the relaxation effect. However, in case of relaxation from the interaction of individual magnetic nuclei, the distance of approach of nuclei to each other (i.e., the distance from the signal-producing nuclei to the dipoles producing the perturbing fields) is limited by atomic radii. In the present calculation, however, it was assumed that the macroscopic magnetic dipoles (magnetic grains) were essentially point sources, with no lower limit to the distance of approach, and correspondingly, no upper limit to the strength of the perturbing field. The field of a dipole becomes so strong at small distances that it is no longer possible to define a correlation time as Bloembergen[10] did.

In the present problem it is still possible to define roughly a time for an element of the sample to become randomly relocated by diffusion, namely the time for diffusion over a distance comparable to the average distance between the magnetic grains. The effect on the signal decay would correspond to an averaging of a number of random choices from a Cauchy distribution of phase shifts. However, the distribution of averages of random choices from a Cauchy distribution is the same Cauchy distribution,[9] not a narrower distribution as for the more familiar Gaussian distribution. Thus, diffusion should have no effect on the result given in Eqs. (15) through (17). Diffusion does provide the possibility that an element of the sample will have the effect of a time spent in a region of positive perturbing field cancelled by a time spent in a negative field. However, this cancellation is offset by the fact that a rapidly diffusing element of the sample has a greater chance of spending a little time in a region very close to one of the magnetic grains, where the field is exceedingly strong. The result is that diffusion has no effect in either direction.

Fulfillment of the Assumptions

The relationship derived above has been applied to several systems of practical interest: porous rock that contains magnetite grains, sand mixed with powdered magnetite, and fluids containing dispersed magnetite powder. The magnetite powder used has a grain size of the order of a micron and retains a magnetization of about 11 emu/gram after exposure to a strong field.

[10] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

Concentrations used were of the order of 10^{-5} by volume. This amounts to about 10^7 particles/cc if there is no clumping. Even with considerable clumping, requirement (a) is well met. Assumption (b) requires only a sample size large compared to the spacing of the magnetic grains (ignoring some possible large-scale inhomogeneous fields), (c) is satisfied for the magnetite dispersed in fluids, but not entirely for the material in sand or rock, where the magnetite is on the rock or sand surfaces. However, the magnetite grain spacing is of the order of pore dimensions, making this constraint a minor one. (d) is subordinate to (e) so long as the field at the edge of a magnetite grain is much greater than the precession field, which it is for low-field work. (e) is justified by the fact that, even with a diffusion constant as high as 10^{-4} cm^2 sec^{-1} and a precession field as low as 0.5 gauss (earth's field), the phases of the precessing nuclei are completely scrambled in a few cycles of precession. Thus, there would be no further effect of even more rapid changing of phase. The effects mentioned in (g) are independent effects, and corrections may be made for them. In particular, signals may be observed for a sample with and without the magnetic grains, with the ratio of the signals giving the signal decay form corresponding to the magnetic grains effect.

EXPERIMENTAL

A sample of water containing 5% by weight of carboxy-methylcellulose (CMC) and a small amount of magnetite powder was stable over long periods of time at temperatures from 0° to 100°C. It showed a permanent magnetization[11] of 8.3×10^{-4} emu/cc after being subjected to any magnetizing field of over one kilogauss. It is assumed that the grains were all magnetized in the same direction. They were subject to a 7-kilogauss field, and furthermore, the particles were free to turn physically to line up with the field. Free precession signals were observed, with the magnetization at about 60° to the precession field (earth's field in this case). The signal decay time was 10.8 ± 0.5 msec at all temperatures between 0° and 100°C. The time computed from (17) is 9.8 msec, about 10% lower than observed. All thermal relaxation times at all field strengths over one gauss were over 1.0 sec.

Magnetite powder was suspended also in glycerine, with a permanent magnetization of 5.6×10^{-4} emu/cc. Free precession signals were observed for this sample and for a sample of pure glycerine, both at 46°C. The magnetite effect is given by the ratio of the signals, which ratio showed a decay time of 14.4 msec. The time computed from (17) is 14.5 msec.

A small amount of powdered magnetite was added to some very clean quartz sand, and the sand was saturated with water. Thermal relaxation times were over 0.1 sec at all temperatures and fields. Signal decay times were 14.0 ± 1.0 msec at temperatures from 0° to 100°C. The measurement was repeated with glycerine instead of water in the pores. At 50°C the signal decay time, corrected for the bulk relaxation rate of the glycerine, was again 14 msec. The signal decay time computed from (17) is 19.0 msec.

The magnetite grains are small compared to the quartz grains, and some are seen by the fluid as lying on convex or plane surfaces, making at least half the space in the immediate vicinity of these magnetite grains accessible to the fluid. Others are in crevices, where only little fluid is close to the grain. However, only about 40% of the space is filled with fluid, and all the magnetic grains are in this 40%, making the concentration in the fluid phase 2.5 times greater than in the sample as a whole. Thus, one might expect a slightly greater effect of the magnetite in the sand than would be obtained in a simple liquid suspension.

A stringent test of the exponential character of the signal decay was made. Signals were observed for a water-magnetite-CMC suspension with a signal decay time of 62 msec and for a clean water sample of the same dimensions. The ratio of the signals was plotted and found to decay exponentially for decay by a factor of 100. The scatter of points was about 10% at the low end of the curve and negligible elsewhere.

It may be noticed from (17) that the free-precession signal decay gives a measurement of the total magnetic moment content of a suitable sample even if the moments of the various grains are not aligned.

THERMAL RELAXATION

For magnetic grains of micron size or over, very little contribution to thermal relaxation is expected. Diffusion is slow enough and precession frequency high enough that changes of magnetic field under diffusion is substantially adiabatic. Little or no contribution to the thermal relaxation was observed for the liquid suspensions, but a moderate contribution was observed for the magnetite and water in clean quartz, the effect increasing with temperature. The effect may well be due to some smaller particles of magnetite produced by abrasion by the quartz.

SUMMARY

If a fluid from which free-precession signals are observed contains randomly distributed magnetic dipoles (such as ferromagnetic grains), the contribution of these dipoles to the signal decay is a factor which is simply exponential in time. The time constant is given by (17) and is almost independent of dipole orientation, random or systematic. The contribution to the signal decay rate is independent of the viscosity or diffusion rate of the fluid.

ACKNOWLEDGMENT

Thanks are due Dr. Z. V. Jizba for a discussion of the properties of the Cauchy distribution.

[11] The remanent magnetization was measured by means of an apparatus which simultaneously magnetizes the sample uniformly and polarizes a water sample. The inhomogeneous field from the magnetized sample causes the free precession signal from water to decay, the decay rate being a measure of the sample magnetization.