THE phenomenological equations of Bloch\(^1\) have played an important role in the development of nuclear magnetic resonance. They have been found to give an excellent description of resonance and associated transient phenomena in the case of single lines in fluids. The purpose of this note is to propose a generalization of the Bloch equations which incorporates effects due to the diffusion of magnetization. Such effects will arise under conditions of inhomogeneity in magnetic field, relaxation rates, or initial magnetization. With the aid of the generalized Bloch equations such problems can be solved with relative ease.

Diffusion of magnetization will generally take place by self-diffusion of moment-bearing nuclei. Another possible mode is spin-direction exchange between neighboring nuclei induced by direct dipolar interaction or by the exchange-coupling via electrons. Diffusion by spin-exchange has been considered by Bloembergen\(^2\) in connection with the effect of impurities on the relaxation time in crystalline solids. In fact he used an equation which can be considered as a specialization of Eq. (3) below. The effective diffusion coefficient for spin-exchange is, as Bloembergen showed, of the order of \(\sigma^2/50T_2\), where \(\sigma\) is the separation of neighbors and \(T_2\) the transverse relaxation time. For fluids, except in the case of very high viscosity, the coefficient of self-diffusion is many orders of magnitude larger than the spin exchange coefficient. Also spin-exchange diffusion may be expected to affect only the longitudinal component (component in direction of instantaneous field). We shall understand by \(D\) the coefficient of self-diffusion and will indicate below what corrections need be made to take spin-exchange into account.

The usual Bloch equations may be thought of as describing the continuity of magnetic moment. Indeed Bloch's original derivation was based on this idea. Thus for example the rate of increase of \(x\) component of magnetic moment is equated to the sum of two parts:

\[\frac{\partial}{\partial t}M_x = n_x V_x - D \nabla n_x,\]

(a) the contribution of the torque exerted by the magnetic field on the vector moment and (b) the contribution of the relaxation processes. Under inhomogeneous conditions we extend this idea to the magnetic moment of an elementary volume \(\Delta\).

Because of the diffusion of magnetization through the surface of \(\Delta\), we must include an additional contribution to the rate of increase of the magnetic moment of \(\Delta\). The diffusion current density of magnetization may be found as follows:

We choose axes arbitrarily oriented with respect to the field direction. Let us quantize the spins along a coordinate axis, say the \(x\) axis, and let \(n_+\) and \(n_-\) be, respectively, the number of positively and negatively oriented spins in this direction. (We are assuming a spin of \(\frac{1}{2}\); the final result is independent of the spin.) The diffusion current densities of the two types will then be

\[i_+ = n_+ V_+ - D \nabla n_+, \quad i_- = n_- V_- - D \nabla n_-\]

Here \(V_+\) (\(V_-\)) is the drift velocity of the positively (negatively) oriented spins.\(^3\) We may assume the drift velocity to be proportional to the force on the nucleus produced by the action of the field gradient on its magnetic moment. The force on a nucleus with a positively oriented spin of moment \(\mu\) will be

\[f_+ = \nabla (\mu \cdot H) = \mu \nabla H_x,\]

since the spin is oriented along the \(x\) axis. Similarly,

\[f_- = -\mu \nabla H_x.\]

If the fluid is confined, there will be a small additional force caused by the fact that the field gradient produces a body force acting on the magnetized medium. A pressure gradient is set up in response and is responsible for an average force of the surroundings on a nucleus. This force is, however, of order \(\mu H/kT\) compared with the direct force \((\nabla \mu \cdot H)\) and will be neglected.

Thus we shall have \(K V_+ = \pm \mu \nabla H_x\), where \(K\) is the conductivity. By Einstein's relation, \(K = kT/D\). The

\(^3\) I am indebted to Professor Lars Onsager for pointing out to me the desirability of including the drift current. Actually, as will be seen below, it is doubtful that the drift terms will produce effects of discernible magnitude.
diffusion currents become

\[ j_x = \pm \frac{\rho}{(kT)n_s} \nabla H_x - D \nabla n_x. \]

The diffusion current of the \( x \) component of magnetization will be given by

\[ \mu(j_x - j_-) = -D \nabla \mu(n_x - n_-) - nD \nabla (\mu H_x/kT) \]

\[ = -D \nabla (M_x - M_{eq}), \]

where \( M_{eq} = (nH/kT)H_x \) is the \( x \) component of the equilibrium magnetization. The rate of increase of \( x \) component of magnetic moment of the volume element \( \Delta v \) due to this diffusion current will thus be

\[ \int (\partial M_x/\partial t)dv = -\int \mu n \cdot (j_x - j_-)dS \]

\[ = \int Dn \cdot \nabla (M_x - M_{eq})dS \]

\[ = \nabla \cdot D \nabla (M_x - M_{eq}) \Delta v. \]

This term must be added to the \( x \) component Bloch equation. Proceeding in a similar way with the other components and dividing by \( \Delta v \), one obtains

\[ \partial M_x/\partial t = \gamma (M \times H)_x - M_x/T_2 + \nabla \cdot D \nabla (M_x - M_{eq}), \]  
\[ \partial M_y/\partial t = \gamma (M \times H)_y - M_y/T_2 + \nabla \cdot D \nabla (M_y - M_{eq}), \]
\[ \partial M_z/\partial t = \gamma (M \times H)_z + (M_z - M_{eq})/T_1 \]
\[ + \nabla \cdot D \nabla (M_z - M_{eq}). \]  

In the case of spin-exchange diffusion (coefficient \( D_e \)), the \( D \) in Eq. (3) needs to be augmented by \( D_e \). These equations differ from the Bloch equations not only by addition of the diffusion terms, but also in that the time derivatives are now partial since they refer to a particular point in space.

It will be recalled that the Bloch equations are intended to refer to the case of a strong field in the \( z \) direction with possible small variable components in the equatorial plane. It would seem at first that for this case we should put \( M_{eq} = M_{eq} = 0 \) and \( M_{eq} = M_{eq} \), the equilibrium magnetization. However, it should be noted that it is the spatial derivatives of \( M_{eq} \) and \( M_{eq} \) that enter into the first two equations. If the magnetic field has a gradient, the gradients of \( M_{eq} \) and \( M_{eq} \) will be of the same order as the gradient of \( M \) and thus the terms in \( M_{eq} \) and \( M_{eq} \) must be included along with the term in \( M_{eq} \). These “drift” terms (terms in \( M_{eq}, M_{eq}, M_{eq} \)) will, however, in general be quite small and their effects almost always negligible. In order for the resonance to be observed even with refocussing techniques, it is necessary that the field gradient be kept very small and thus the gradients in \( (M_{eq}, M_{eq}, M_{eq}) \) also is very small. In spite of this condition it is possible to have very large gradients in the actual magnetization \( M \). There may, for example, be sharp gradients in \( T_1 \) and \( T_2 \) so that relaxation proceeds at quite different rates at localities a short distance apart. A second possibility for large gradients in the magnetization arises when the magnetization is disoriented from the field direction. The magnetization then precesses about the field. If the field has even a very small gradient, the cumulative effect of slight differences in precession rate at neighboring localities will eventually produce large gradients in the magnetization. In the second part of this paper the generalized Bloch equations are applied to this effect.

Equations (1)–(3) refer, as do the usual Bloch equations, to the case of a large static field \( H_0 \) in the \( z \) direction plus possible small components which may be variable in the equatorial plane. The usual Bloch equations can be modified so that transverse relaxation takes place perpendicular, and longitudinal relaxation parallel to the instantaneous magnetic field. The equations thus modified apply to a general magnetic field. Written in vector notation without reference to a coordinate system, the modified equations generalized by the diffusion and drift terms would take the form

\[ \partial M/\partial t = \gamma (M \times H) - M/T_2 + \chi H/T_1 + (M \cdot H_0/H^2) \]
\[ \times (1/T_1 - 1/T_2) + \nabla \cdot D \nabla (M - M_0). \]  

In case spin-exchange diffusion is not negligible, an additional term \( \nabla \cdot D \nabla (M - M_0) \cdot H_0/H^2 \) needs to be added to the right side of (4).

This refinement (4) of (1)–(3) is inconsequential if, as is usually the case, the line width is small compared with the resonant frequency.

Since the drift terms are very small for the reasons given above, we shall omit them in the example treated in Sec. II.

II

As an example, we shall now apply Eqs. (1) and (2) to find the spin-echo amplitudes in the presence of an inhomogeneous field. This problem has been treated by different methods by Hahn,\(^4\) by Das and Saha,\(^5\) and by Carr and Purcell.\(^6\) We shall assume with the latter authors that a field 90° disorienting pulse is followed by a succession of 180° pulses. The procedure adopted here is more general and less cumbersome than prior methods.

We assume that the magnetic field consists of (a) a uniform magnetic field \( H_0 \) in the \( z \) direction and (b) a superposed field vanishing at the origin with gradient \( G \) in the \( z \) direction and with axial symmetry about the \( z \) axis. The most general resultant field of this character, linear in the coordinates, is (neglecting contributions arising from \( M \))

\[ H_x = -\frac{1}{2} G_x, \quad H_y = -\frac{1}{2} G_y, \quad H_z = H_0 + G_z. \]  

---

We now substitute (5) in (1) and (2), multiply the resulting equation (2) by \( i = (-1)^{1/2} \) and add to (1). Defining
\[
m = m_0 + im_1,
\]
we obtain
\[
\frac{\partial m}{\partial t} = -i\omega_0 m - i\gamma G_2 m - m/T_2 + \nabla \cdot D \nabla m
\]
(7)
\[
-\frac{1}{2}i\gamma G(x+iy)M_e.
\]
Here \( \omega_0 = \gamma H_0 \) and \( m \), the complex transverse magnetization, is a vector in the complex \( x-y \) plane which precesses about the \( z \) axis with angular speed \( -\omega_0 \). In the absence of diffusion, \( m \) is exponentially damped with relaxation time \( T_2 \). Putting
\[
m = e^{-i\omega t - it/T_2},
\]
we obtain from (7) and (8)
\[
\frac{\partial \varphi}{\partial t} = -i\gamma G_2 \varphi - \frac{1}{2}i\gamma G(x+iy)Me^{i\omega t + i/T_2} + \nabla \cdot D \nabla \varphi.
\]
(9)

The second term on the right oscillates rapidly and contributes to \( \varphi \) an amount of order \( M_e G(x+iy)/H_0 \) which we assume to be negligible. Dropping this term, we have then
\[
\frac{\partial \varphi}{\partial t} = -i\gamma G_2 \varphi + \nabla \cdot D \nabla \varphi.
\]
(10)
\[\varphi = M_0 A(t) e^{-i\gamma G t}, \]
(11)
where \( A(t) \) is a function of \( t \) only. This assumption will hold so long as the diffusion time of a nucleus to the boundaries of the material is long compared with the damping time.

Substituting (11) in (10), we obtain
\[
\frac{dA}{dt} = AD\gamma G^2 \varphi - AD_\gamma G^2 \varphi
\]
(12)
\[\frac{dA}{dt} = \frac{1}{2}AD_\gamma G^2 \varphi.
\]
Integration gives, since \( A(0) = 1 \),
\[A = \exp \left( -\frac{1}{2}AD_\gamma G^2 t \right), \]
(13)
which is the well-known result for the attenuation by diffusion following a 90° pulse.

We now investigate the effect of applying a series of 180° pulses at times \( t_1, 3t_1, 5t_1, \text{etc.} \), after the 90° pulse. Just before the first 180° pulse, the phase of \( \varphi \) by (11) is \( -\pi = -\gamma G t_1 \). The first 180° pulse rotates the magnetization about an axis in the equatorial plane perpendicular to the axis of zero phase, thus shifting the phase of \( \varphi \) to \( \pi + \delta \). During the subsequent interval \( 2t_1 \), the phase shifts to \( \pi - \delta \) and the second 180° pulse shifts the phase to \( +\delta \). The next interval of \( 2t_1 \) brings the phase again back to \( -\delta \) and the process repeats. Just after the \( n \)th 180° pulse, the phase is \( \pi + \delta \) if \( n \) is odd and \( +\delta \) if \( n \) is even. Whenever the phase is 0 or \( \pi \), i.e., at \( \pi = 2nt_1 \), there is an echo. Thus, within the period of duration \( 2t_1 \) following the \( n \)th pulse, we have, if \( n \) is even,
\[\varphi = M_0 A(t) \exp \{i\gamma G t_1 - i\gamma G t(2n-1)t_1]\]
(14)
and if \( n \) is odd,
\[\varphi = M_0 A(t) \exp \{i\gamma G t(2n-1)t_1\}.
\]
(15)

Substituting either (13) or (14) in (10), we obtain
\[
\frac{dA}{dt} = -AD_\gamma G^2 t(2n-1)t_1.
\]
Integrating from \( (2n-1)t_1 \) to \( t \), we get
\[A(t) = A[(2n-1)t_1] \exp \{ -\frac{1}{2}AD_\gamma G^2 [t(2n-1)t_1^2 + t_1^2] \}.
\]
(16)
Thus, at the end of the interval,
\[A(t) = A[(2n-1)t_1] \exp \{ -\frac{1}{2}AD_\gamma G^2 t_1^2 \}.
\]
(17)

It follows that each interval attenuates the amplitude by \( \exp \{ -\frac{1}{2}AD_\gamma G^2 t_1^2 \} \). Since the interval between the 90° pulse and the first 180° pulse attenuates by \( \exp \{ -\frac{1}{2}AD_\gamma G^2 t_1^2 \} \), we get
\[A[(2n-1)t_1] = \exp \{ -\frac{1}{2}(2n-1)AD_\gamma G^2 t_1^2 \}.
\]
(18)
Substituting (17) in (16) and putting \( t = 2nt_1 \), we find for the amplitude of the \( n \)th echo
\[A(2nt_1) = \exp \{ -\frac{1}{2}AD_\gamma G^2 t_1^2 \} ;
\]
or, putting \( t_1 = t/2n \),
\[A(t) = \exp \{ -\frac{1}{2}AD_\gamma G^2 t/12n^2 \},
\]
(19)
which is precisely the result of Carr and Purcell obtained by them from a random walk theory.

Equation (18) may be written in the form
\[A(t) = \exp \{ -\frac{1}{2}AD_\gamma G^2 t/12n^2 \}.
\]
(20)
Substituting (19) and (11) in (8), it is seen that the echo amplitudes decay exponentially with relaxation time \( T_2 \) given by
\[1/T_2 = 1/T_2 + \frac{1}{2}AD_\gamma G^2 t_1^2.
\]
(21)
The final result, (18) or (19), does not depend on the assumption made above that the rotating \( rf \) field component maintains a certain fixed direction from pulse to pulse in the rotating frame of reference. Indeed it may easily be seen that \( H_1 \) may have any orientation in the equatorial plane and that this direction may vary from pulse to pulse without affecting the key equation (15).