Use of Spin Echoes in a Pulsed Magnetic-Field Gradient to Study Anisotropic, Restricted Diffusion and Flow*

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The Bloch–Torrey equations are modified to include the case of anisotropic, restricted diffusion and flow. The problem of solving these modified equations for the amplitude of a spin echo in a time-dependent magnetic-field gradient subject to restricting boundary conditions is discussed. This problem is solved for a number of selected cases. In particular, it is found that a magnetic-field gradient applied in short, intense pulses is effective in defining the time during which nuclear displacements take place. A simplified equation, suitable for the pulsed-gradient experiment, is presented and solved for two different examples of systems showing restricted diffusion. A procedure for analyzing the data from pulsed-gradient measurements is suggested, and its merits are discussed. Suggestions are made of systems which may well be expected to show restricted, anisotropic diffusion or interesting flow properties.

INTRODUCTION

IT has been observed by Woessner[1]—while making measurements of self-diffusion coefficients in certain solid and semisolid systems by means of the spin-echo method of Hahn,[2,3] Carr and Purcell,[4] and others[5]—that the apparent diffusion coefficient which he measured was a function of the parameters of the experiment. In particular the diffusion coefficient was dependent upon the time τ separating the 90° pulse and the 180° pulse. He attributed this effect to the fact that, in the systems studied (water diffusing around silica particles and benzene diffusing through rubber), the diffusing molecules were not able to travel for an appreciable distance without either running up against a deflecting barrier or venturing into a region of decreased mobility. The result was that, as τ was decreased, the behavior began to approach that of the pure liquid while for longer τ the effective diffusion coefficient decreased. One of the difficulties arising in an attempt to treat Woessner's data quantitatively stems from the nature of the spin-echo self-diffusion measurement. Between the 90° pulse and the echo, all molecular displacements contribute something to the attenuation of the echo but with a weighting which depends on where within this time interval the displacement takes place. Displacements are particularly effective near the 180° pulse. An experiment which permits a simpler interpretation will be an aid in defining this problem for a theoretical treatment.

Studies of spin echoes in a time-dependent magnetic-field gradient have been pursued for several different advantages. Anderson, Garwin, Hahn, Horton, Tucker, and Walker[6] have employed time-dependent gradients in an information-storage device. As pointed out by McCall, Douglass, and Anderson,[7] proper use of a time-dependent field gradient may have advantages in the measurement of diffusion coefficients. In the first paper of this series,[8] we have developed and tested this last idea. The particular choice of time-dependent gradient considered in detail was such that the gradient was small at the time of the rf pulses and also at the time of the echo and arbitrarily large elsewhere. Thus the resonance linewidth is small at the time of the rf pulses and the echo. In consequence, H_1 need not be particularly large; and the echo is broad, permitting a more precise measurement of its amplitude. The principal advantage to be obtained is in the measurement of very small diffusion coefficients. However, as was noted in this earlier work, if the gradient is applied in very short pulses, there is an increased precision in the definition of the time allowed for diffusion. The purpose of this paper is to explore this point more fully.

By way of discussing the problem of restricted diffusion, we consider in detail the effect of motion of the resonant nuclei on the nuclear magnetic resonance experiment by means of a suitable modification of the Bloch–Torrey equations.[9–11] We consider the possibility of a time-dependent, space-dependent, anisotropic diffusion coefficient as well as time-dependent, space-

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dependent flow.[12] Restrictive boundary conditions are also discussed. After developing an expression applicable to any gradient variation so long as diffusion and flow are uniform throughout the system, the pulsed gradient is introduced and an expression developed capable of coping with the problem of restricted diffusion. Two cases are treated in detail: the case of diffusion near an attractive center and the case of diffusion within a laminar system. Finally, the problem of analyzing and interpreting the data from a system of unknown internal structure showing evidence of restricted diffusion is discussed.

MODIFIED BLOCH-TORREY EQUATIONS

Torrey[10] has generalized the phenomenological equations of Bloch[9] to include the effect of diffusion of the spins. In order to treat the case of anisotropic, restricted diffusion and also flow we modify Torrey's approach. Consider the change in magnetic moment within an element of volume ΔV. Choose a set of coordinate axes oriented arbitrarily with respect to the field direction. We quantize the nuclear spins along a particular axis, say the x axis. Writing in a single expression the diffusion current densities $\mathbf{j}_+$ and $\mathbf{j}_-$ representing, respectively, the flux of spins oriented toward the positive and negative x directions (we assume a spin of $\frac{1}{2}$ but expect the results to be independent of the spin), we obtain:

$$\mathbf{j}_\pm = \mathbf{v}n_\pm - \mathbf{D}\cdot\nabla n_\pm,$$

where $n_\pm$ represents the densities of either the positively or negatively oriented spins and $\mathbf{v}$ the velocity of the spins due to the flow of the medium within which they are imbedded. $\mathbf{D}$ is the diffusion tensor and accounts for diffusion within and relative to the moving medium. Both $\mathbf{v}$ and $\mathbf{D}$ may be functions of both position and time. We have omitted the term representing the drift velocity included by Torrey on the grounds that its effect is small,[10] especially when the magnetic-field gradient is applied in short (compared to T_1) pulses.[8] The diffusion current density of magnetization is written as

$$\mu(\mathbf{j}_+ - \mathbf{j}_-) = \mathbf{v}M_x - \mathbf{D}\cdot\nabla M_x,$$

since

$$\mu(n_+ - n_-) = M_x,$$

where $\mu = \hbar\gamma I$ represents the magnetic moment of a single spin and M_x the x component of the magnetic moment per unit volume. Consider the flux through the element of volume ΔV:

$$\left(\frac{\partial M_x}{\partial t}\right)_{\mathrm{D,v}} = \frac{-1}{\Delta V}\int_S \mu(\mathbf{j}_+ - \mathbf{j}_-)\cdot d\boldsymbol{\delta}$$

$$= \frac{1}{\Delta V}\int_S (-\mathbf{v}M_x + \mathbf{D}\cdot\nabla M_x)\cdot d\boldsymbol{\delta}$$

$$= -\nabla\cdot\mathbf{v}M_x + \nabla\cdot\mathbf{D}\cdot\nabla M_x.$$

[12] R. J. Blume, Rev. Sci. Instr. **30**, 41 (1959), discusses several examples of spin echoes observed in flowing systems.

The last step was completed through the application of the divergence theorem. The other two components of the nuclear magnetization $\mathbf{M}$ may be computed in a like manner with the result that the Bloch equations may be written (as modified):

$$\frac{\partial \mathbf{M}}{\partial t} = \gamma\mathbf{M}\times\mathbf{H} - \frac{(M_x\hat{\imath} + M_y\hat{\jmath})}{T_2} + \frac{(M_0 - M_z)\hat{k}}{T_1}$$

$$-\nabla\cdot\mathbf{v}\mathbf{M} + \nabla\cdot\mathbf{D}\cdot\nabla\mathbf{M}. \quad (1)$$

If desired, the "drift" terms of Torrey may be also inserted into this expression.

SPIN ECHOES IN A TIME-DEPENDENT FIELD GRADIENT

The form of Eq. (1) requires that the applied magnetic field $\mathbf{H}$ consist of a large component applied along the z axis and possibly small fluctuating components in the x–y plane. Accordingly we define an applied magnetic-field gradient $\mathbf{G}$ by means of the expression[8,10,11]

$$\mathbf{H} = [H_0 + (\mathbf{r}\cdot\mathbf{G})]\hat{k}, \quad (2)$$

where $\mathbf{G}(t)$ is assumed to be uniform throughout the sample. Properly speaking such a unidirectional field cannot exist, since $\nabla\cdot\mathbf{H}\neq 0$, however, we consider the z axis to lie along the actual direction of the local applied field. Changes in $\mathbf{G}$ which alter this direction are assumed to be adiabatic. Substituting Eq. (2) into Eq. (1) and inquiring after the behavior in the x–y plane by means of the quantity $m = M_x + iM_y$ we obtain

$$\partial m/\partial t = -i\omega_0 m - i\gamma\mathbf{r}\cdot\mathbf{G}m - (m/T_2)$$

$$-\nabla\cdot\mathbf{v}m + \nabla\cdot\mathbf{D}\cdot\nabla m, \quad (3)$$

where $\omega_0 = \gamma H_0$. Next we transform to a coordinate system rotating about the z axis with angular velocity ω_0 in the same sense as $\mathbf{M}$ precesses. We allow for the transverse relaxation process (T_2 decay) at the same time by defining $\psi(\mathbf{r}, t)$ by means of the expression

$$m = \psi\exp\{-[i\omega_0 + (1/T_2)]t\}.$$

Substitution into Eq. (3) yields

$$\partial\psi/\partial t = -i\gamma\mathbf{r}\cdot\mathbf{G}\psi - \nabla\cdot\mathbf{v}\psi + \nabla\cdot\mathbf{D}\cdot\nabla\psi. \quad (4)$$

If Eq. (2) is modified so as to make $\nabla\cdot\mathbf{H} = 0$, there will be additional terms in Eq. (4). These will oscillate rapidly and may be neglected.[10]

We wish to solve Eq. (4) for ψ to find the effects of $\mathbf{D}$, $\mathbf{v}$, and whatever boundary conditions need to be imposed. We prefer to impose spatial boundary conditions by means of the position dependence of $\mathbf{D}$ and $\mathbf{v}$ if convenient. On the other hand, the restrictions on the time dependence of ψ resulting from the rf pulses will be imposed directly. Since we have been unable to find a general solution, i.e., valid for any $\mathbf{G}(t)$, for

Eq. (4) for any example in which either **D** or **v** is position-dependent, we restrict ourselves to **D** and **v** dependent only on time and defer the more general problem until our discussion of the pulsed gradient.

Consider Eq. (4) without the **D** and **v** terms. This truncated equation is solved by

$$\psi = A\exp[-i\gamma\mathbf{r}\cdot(\mathbf{F}-2\zeta\mathbf{f})+i\zeta(2\phi-\pi)], \quad (5)$$

where

$$\zeta=0 \quad \text{for} \quad 0<t<\tau,$$

$$\zeta=1 \quad \text{for} \quad t>\tau,$$

$$\mathbf{F}(t)=\int_0^t \mathbf{G}dt', \quad \text{and} \quad \mathbf{f}=\mathbf{F}(\tau),$$

and where we have imposed the boundary conditions that $\psi=A$ immediately following the 90° pulse (along the negative y axis in the rotating frame) at $t=0$ and that the effect of a 180° pulse (with a phase angle ϕ relative to the 90° pulse) at $t=\tau$ is to turn $\psi(\mathbf{r},\tau)$ into $\psi^*(\mathbf{r},\tau)\exp[i(2\phi-\pi)]$.

Next we reintroduce the $\mathbf{v}(t)$ term to Eq. (4). We seek to solve the resulting equation by means of the substitution

$$A(t)=B\exp[i\Phi(t)]. \quad (6)$$

The equation which Φ must satisfy is obtained by introducing the above expression into Eq. (5) and the combined expression into the partially restored form of Eq. (4):

$$d\Phi/dt=\gamma\mathbf{v}\cdot(\mathbf{F}-2\zeta\mathbf{f}).$$

The solution to this expression may be written in either of two convenient forms

$$\Phi=\gamma[K-2\zeta\mathbf{f}\cdot(\mathbf{S}-\mathbf{s})-2\zeta k],$$

or

$$\Phi=\gamma[\mathbf{S}\cdot(\mathbf{F}-2\zeta\mathbf{f})-H+2\zeta h], \quad (7)$$

where

$$\mathbf{S}(t)=\int_0^t \mathbf{v}dt', \qquad \mathbf{s}=\mathbf{S}(\tau),$$

$$K(t)=\int_0^t \mathbf{v}\cdot\mathbf{F}dt', \qquad k=K(\tau),$$

$$H(t)=\int_0^t \mathbf{S}\cdot\mathbf{G}dt', \quad \text{and} \quad h=H(\tau).$$

The two forms are the result of the fact that

$$K\equiv\mathbf{S}\cdot\mathbf{F}-H,$$

as may be verified by differentiation and also checking this identity at $t=0$. It should be noted that the boundary conditions detailed earlier are still satisfied by the expression for ψ including Φ. A point must be made in connection with the experimental conditions which must prevail in a flowing system.[12] It is assumed in the above discussion that the nuclei which we observe have all been subjected equally to the prescribed pulses. Thus H_1 will have to extend over a large enough volume to include those nuclei which have not yet reached the point at which they will be detected.

Only one term remains to be reinserted into Eq. (4), the term involving $\mathbf{D}(t)$. The effect of this term will be absorbed by allowing B to be a function of t (only). Substitution into the now complete form of Eq. (4) yields the following equation for $B(t)$:

$$d\ln B/dt=-\gamma^2(\mathbf{F}-2\zeta\mathbf{f})\cdot\mathbf{D}\cdot(\mathbf{F}-2\zeta\mathbf{f}).$$

This equation integrates directly to yield

$$\ln[B(t)/B(0)]$$

$$=-\gamma^2\left(\int_0^t \mathbf{F}\cdot\mathbf{D}\cdot\mathbf{F}dt'-4\zeta\int_\tau^t \mathbf{F}\cdot\mathbf{D}\cdot\mathbf{f}dt'+4\zeta\int_\tau^t \mathbf{f}\cdot\mathbf{D}\cdot\mathbf{f}dt'\right), \quad (8)$$

where we have made use of the fact that **D** will be symmetric. In the event that **D** is constant with time, this expression may be shortened somewhat;

$$\ln[B(t)/B(0)]$$

$$=-\gamma^2\left[\int_0^t \mathbf{F}\cdot\mathbf{D}\cdot\mathbf{F}dt'-4\zeta\mathbf{f}\cdot\mathbf{D}\cdot\int_\tau^t \mathbf{F}dt'+4\zeta\mathbf{f}\cdot\mathbf{D}\cdot\mathbf{f}(t-\tau)\right].$$

We may now gather Eq. (5), Eq. (6), and Eq. (7) together into a single expression for $\psi(\mathbf{r},t)$

$$\psi=B(t)$$

$$\times\exp\{-i\gamma[(\mathbf{r}-\mathbf{S})\cdot(\mathbf{F}-2\zeta\mathbf{f})+H-2\zeta h]+i\zeta(2\phi-\pi)\},$$

where $B(t)$ is obtained from Eq. (8). A general description of the behavior of the system may now be obtained by integrating ψ over the entire system, weighting each portion in proportion to its contribution to the observed signal. While any maximum in the observed signal may be called an echo, we define the principal echo as that which occurs when $t=\tau'$ defined by

$$\mathbf{F}(\tau')-2\zeta\mathbf{f}=0.$$

When this occurs (if it ever does) ψ becomes independent of $\mathbf{r}$ and there is no need to integrate over the sample:

$$\psi(\tau')=B(\tau')\exp\{-i\gamma[H(\tau')-2\zeta h]+i\zeta(2\phi-\pi)\}. \quad (9)$$

Thus we observe that the effect of diffusion on the principal echo is to attenuate its amplitude and that the effect of flow is to shift its phase.

PULSED GRADIENT

In order to illustrate the use of Eq. (9) and also prepare for the development of an approach to more

complex types of diffusion we treat the case of a particular $\mathbf{G}(t)$. Let $\mathbf{G}(t)$ equal[8]:

$$\begin{aligned}
&\mathbf{g}_0 && \text{when} \quad 0<t<t_1,\\
&\mathbf{g}_0+\mathbf{g} && \text{when} \quad t_1<t<t_1+\delta<\tau,\\
&\mathbf{g}_0 && \text{when} \quad t_1+\delta<t<t_1+\Delta>\tau,\\
&\mathbf{g}_0+\mathbf{g} && \text{when} \quad t_1+\Delta<t<t_1+\Delta+\delta<2\tau,\\
&\mathbf{g}_0 && \text{when} \quad t_1+\Delta+\delta<t.
\end{aligned}$$

Furthermore, we are interested in the limit as $\mathbf{g}_0\to 0$ and $\delta\to 0$ while $\delta\mathbf{g}$ remains finite. We refer to this as the case of the pulsed gradient. As long as $\mathbf{g}_0$, which represents the imperfections in the laboratory field, has not quite vanished, we shall find the echo at $\tau'=2\tau$.[8] Consequently, we fix our attention on that point. The experimental technique required for the production of intense, short pulses of magnetic field gradient is discussed elsewhere.[8,13] For simplicity we also assume that $\mathbf{D}$ is constant. We obtain for a result

$$\psi(2\tau)=B(0)\times\exp[-\gamma^2\delta^2\mathbf{g}\cdot\mathbf{D}\cdot\mathbf{g}\Delta-i\gamma\delta\mathbf{g}\cdot\mathbf{S}(\Delta)+i(2\phi-\pi)], \quad (10)$$

where we have written $\mathbf{S}(\Delta)$ in place of $\mathbf{S}(t_1+\Delta)-\mathbf{S}(t_1)$, which represents the total displacement of the system during the time interval t_1 to $t_1+\Delta$. We may view this experiment in the following way.[8] In the absence of a gradient, there is no loss of phase coherence in the nuclear signal following the 90° pulse. At the time of the first gradient pulse, there is a nearly instantaneous phase shift depending upon the location of each nucleus—a phase shift which may be said to record its position along $\mathbf{g}$. Following the gradient pulse, this phase shift persists until it is inverted by the 180° pulse. The next phase change occurs at the time of the second gradient pulse. A nucleus which has not moved between the gradient pulses or one which has returned to its starting point (viewed along $\mathbf{g}$) is refocused perfectly. Net motion results in incomplete refocusing. We thus have a procedure for detecting net motion during a controlled interval Δ. Since Δ may be of the order of 1 msec, we are speaking of a time interval orders of magnitude shorter than is usually available in diffusion studies involving some form of chemical analysis. Restricted diffusion effects may very well be expected to become visible.

Because of the simple interpretation which exists for the pulsed gradient experiment, it is possible to construct an expression which predicts the result of this experiment and which may be expected to be more tractable in some problems involving restricted diffusion. We modify the analysis of McCall, Douglass, and Anderson[7] for the steady-gradient experiment to obtain

$$\psi(2\tau)=B(0)\exp[i(2\phi-\pi)]\int_{V_0}P_0(\mathbf{r}_0)\int_V P(\mathbf{r}_0\mid\mathbf{r},\Delta)\times\exp[-i\gamma\delta(\mathbf{r}-\mathbf{r}_0)\cdot\mathbf{g}]dVdV_0, \quad (11)$$

where $\psi(2\tau)$ might with equal validity but different emphasis be written $\psi(\mathbf{g},\Delta)$. We define $P(\mathbf{r}_0\mid\mathbf{r},\Delta)$ as the probability that a nucleus initially at position $\mathbf{r}_0$ (at the time of the first gradient pulse) will have migrated to position $\mathbf{r}$ at the time of the second gradient pulse (a time Δ later).[14] An analysis similar to that given earlier reveals that $P(\mathbf{r}_0\mid\mathbf{r},t)$ will satisfy the equation

$$\partial P/\partial t=-\nabla\cdot\mathbf{v}P+\nabla\cdot\mathbf{D}\cdot\nabla P \quad (12)$$

subject to the boundary condition that P is a delta function at $\mathbf{r}_0$ for $t=0$ in addition to the other natural boundary conditions required by the problem. The exponential factor appearing in the integral over V represents the phase change resulting from a migration from $\mathbf{r}_0$ to $\mathbf{r}$. If the integral over V is independent of $\mathbf{r}_0$, the integral over V_0 may be omitted; if not, $P_0(\mathbf{r}_0)$, which indicates the probability of a particular $\mathbf{r}_0$, is used to account for the distribution of starting points. Often it will be the case that

$$P_0(\mathbf{r}_0)=\lim_{t\to\infty}P(0\mid\mathbf{r}_0,t).$$

The solution of Eq. (12) and the evaluation of Eq. (11) may be easier than the direct solution of Eq. (4) even for the pulsed gradient.

For the case of a uniform, constant diffusion tensor and a spatially uniform but time-dependent flow, Eq. (12) has as its solution[14]

$$P(\mathbf{r}_0\mid\mathbf{r},t)=(64\pi^3D_{xx}D_{yy}D_{zz}t^3)^{-\frac{1}{2}}\times\exp\left[-\frac{(x-x_0-S_x)^2}{4D_{xx}t}-\frac{(y-y_0-S_y)^2}{4D_{yy}t}-\frac{(z-z_0-S_z)^2}{4D_{zz}t}\right], \quad (13)$$

where we have chosen to orient our coordination system along the principal axes of the diffusion ellipsoid. The result of substituting this expression into Eq. (11) is Eq. (10), as it must be.

RESTRICTED DIFFUSION

Next, we take up two examples of systems which do not follow the usual laws of diffusion but rather give evidence of restricted diffusion. Other examples which

[13] J. E. Tanner, Rev. Sci. Instr. **36**, 1086 (1965). See also: J. E. Tanner, Ph.D. thesis, University of Wisconsin (in preparation).

[14] M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945), which may be found reprinted in: *Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, Inc., New York, 1954), along with several other pertinent articles.

might have been employed may be found in the literature of heat diffusion.[15]

Diffusion Near An Attractive Center

Suppose we have a particle diffusing in an isotropic medium according to the usual diffusion law, and this particle is subject to an additional force which pulls it toward the origin in proportion to its distance from the origin.[14] For instance a potential function $V=\frac{1}{2}\beta f r^2$ gives rise to a force $\mathbf{F}=-\beta f\mathbf{r}$. In a viscous fluid such a force results in a terminal velocity defined by $\mathbf{F}=f\mathbf{v}$, where f is the friction coefficient. By replacing $\mathbf{v}$ by $-\beta\mathbf{r}$ and writing D as a scalar in Eq. (12) we obtain the following equation for $P(\mathbf{r}_0 \mid \mathbf{r}, t)$:

$$\partial P/\partial t=\beta\nabla\cdot\mathbf{r}P+D\nabla^2P,$$

which is solved by[14]

$$P(\mathbf{r}_0 \mid \mathbf{r}, t)=[2\pi D(1-e^{-2\beta t})/\beta]^{-\frac{3}{2}} \exp[-\beta(\mathbf{r}-\mathbf{r}_0e^{-\beta t})^2/2D(1-e^{-2\beta t})], \quad (14)$$

and where

$$P_0(\mathbf{r}_0)=\lim_{t\to\infty}P(0 \mid \mathbf{r}_0, t)=(2\pi D/\beta)^{-\frac{3}{2}}\exp(-\beta r_0^2/2D).$$

Substitution into Eq. (11) produces the result

$$\psi(\mathbf{g}, \Delta)=B(0)\exp[-\gamma^2\delta^2g^2D(1-e^{-\beta\Delta})/\beta+i(2\phi-\pi)]. \quad (15)$$

This result has some features worth pointing out in comparison to Eq. (10). Write Eq. (10) without $\mathbf{S}$ and for isotropic D:

$$\psi(\mathbf{g}, \Delta)=B(0)\exp[-\gamma^2\delta^2g^2D\Delta+i(2\phi-\pi)]. \quad (16)$$

First we note that the $\mathbf{g}$ dependence is the same in both instances. This is the consequence of P being a Gaussian in both cases. On the other hand the dependence on Δ shown in the two relations immediately above is strikingly different. If we analyze data produced in accordance with Eq. (15) by means of Eq. (16), we arrive at an effective value for D which proves to be a function of Δ;

$$D_{\text{eff}}=D(1-e^{-\beta\Delta})/\beta\Delta.$$

Note that in the limit $\Delta\to 0$ we find $D_{\text{eff}}\to D$ while as $\Delta\to\infty$ the result is that $D_{\text{eff}}\to 0$. For small Δ, where the diffusing particles seldom move a distance to compare with the extent of the occupied portion of the restraining potential-energy well, we are measuring diffusion as if it were free. For large Δ there is a limit as to how far a particle is likely to diffuse. Note that as $\Delta\to\infty$ even though $D_{\text{eff}}\to 0$ the echo amplitude merely levels off:

$$\lim_{\Delta\to\infty}\psi(\mathbf{g}, \Delta)=B(0)\exp[-\gamma^2\delta^2g^2D/\beta+i(2\phi-\pi)].$$

Diffusion in a Laminar System

For our second example of restricted diffusion, we choose a sample in the form of a thin layer. Although infinite in two dimensions, there is a finite thickness a. Within the layer, diffusion follows the usual diffusion law with an isotropic D. For simplicity we assume that a is so small that even for the smallest value of Δ to be considered the probability distribution perpendicular to the layer is uniform and stays that way (i.e., $\Delta\gg a^2/2D$). We write down the following expressions for $P(\mathbf{r}_0 \mid \mathbf{r}, \Delta)$:

$$P(\mathbf{r}_0 \mid \mathbf{r}, \Delta)=(4\pi aD\Delta)^{-1}\exp[-(\mathbf{r}-\mathbf{r}_0)_{||}^2/4D\Delta]$$

inside the layer

$$=0 \qquad \text{outside the layer,} \quad (17)$$

where we use $||$ as a subscript to identify the component parallel to the layer. $P_0(\mathbf{r}_0)$ corresponds to a uniform distribution everywhere within the layer. From these beginnings we obtain

$$\psi(\mathbf{g}, \Delta)=B(0)[2(1-\cos\gamma\delta g_\perp a)/\gamma^2\delta^2g_\perp^2a^2] \times\exp[-\gamma^2\delta^2g_{||}^2D\Delta+i(2\phi-\pi)], \quad (18)$$

where we have used $\perp$ as a subscript to identify the component perpendicular to the layer. If we compare Eq. (18) with Eq. (10) written without $\mathbf{S}$ and for a diffusion ellipsoid in the form of a symmetric top with the unique axis perpendicular to the layer, i.e.,

$$\psi(\mathbf{g}, \Delta) =B(0)\exp[-\gamma^2\delta^2g_{||}^2D_{||}\Delta-\gamma^2\delta^2g_\perp^2D_\perp\Delta+i(2\phi-\pi)], \quad (19)$$

we see opportunities for confusion. If we should perform a series of measurements in which only the direction of $\mathbf{g}$ is varied (Δ and the magnitude of $\mathbf{g}$ unchanged) where the situation is properly covered by Eq. (18) but where $\gamma\delta g_\perp a\ll 1$, we shall not be able to distinguish the observed behavior from a situation covered by Eq. (19) for which $D_\perp=a^2/12\Delta$. Indeed we may even vary $g_\perp$ within the restriction $\gamma\delta g_\perp a\ll 1$ without being able to distinguish these two cases. On the other hand, a thorough study of ψ as a function of Δ and $\mathbf{g}$ (both magnitude and direction) will clearly disclose the differences between Eq. (18) and Eq. (19). Certain features of Eq. (18) are worth noting. The dependence upon $g_\perp$ is peculiar in two ways. Since the distribution function $P(\mathbf{r}_0 \mid \mathbf{r}, \Delta)$ observed perpendicular to the layer is non-Gaussian, the dependence upon $g_\perp$ does not follow the form observed heretofore. Note that ψ goes through a series of nulls, one occurring

[15] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, London, 1959), 2nd ed.

each time $\cos\gamma\delta g_\perp a = 1$ (except at $g_\perp = 0$). Furthermore there is no dependence upon Δ observed for the term involving $g_\perp$. This last property is the result of the fact that we left such dependence out of $P(\mathbf{r}_0 \mid \mathbf{r}, \Delta)$.

ANALYSIS OF PULSED GRADIENT DATA

It may be the case that Eq. (11) can be evaluated without need for $P_0(\mathbf{r}_0)$ or the integral over V_0. In that case we may define

$$\Xi(\mathbf{g}, \Delta) = \psi(\mathbf{g}, \Delta)/B(0) \exp[i(2\phi - \pi)]$$

in which case

$$\Xi(\mathbf{g}, \Delta) = \int_V P(\mathbf{r}_0 \mid \mathbf{r}, \Delta) \exp[-i\gamma\delta(\mathbf{r} - \mathbf{r}_0)\cdot\mathbf{g}]dV.$$

Since Ξ is not a function of $\mathbf{r}_0$ we may choose $\mathbf{r}_0 = 0$ and write

$$\Xi(\mathbf{g}, \Delta) = \int_V P_a(\mathbf{r}, \Delta) \exp(-i\gamma\delta\mathbf{r}\cdot\mathbf{g})dV$$

where we define $P_a(\mathbf{r}, \Delta) = P(0 \mid \mathbf{r}, \Delta)$. This expression may be inverted by means of a Fourier transform.

$$P_a(\mathbf{r}, \Delta) = \left(\frac{\gamma\delta}{2\pi}\right)^3 \int \Xi(\mathbf{g}, \Delta) \exp(+i\gamma\delta\mathbf{r}\cdot\mathbf{g})dg_x dg_y dg_z, \tag{20}$$

where the integral is performed over the entire $\mathbf{g}$ space. For instance, Eq. (13) (without $\mathbf{r}_0$) may be obtained from Eq. (10) (in the principal axis system) since $\mathbf{r}_0$ has no particular significance to the diffusion or flow in this system, i.e., the probability of a particular displacement is independent of $\mathbf{r}_0$.

In many cases this condition of independence of $\mathbf{r}_0$ is not met. Nonetheless, since Ξ is a function of only $\mathbf{g}$ and Δ, it may be treated as if this condition were met. We are thus tempted to use Eq. (20) to obtain a $P_a(\mathbf{r}, \Delta)$ as an approximation to $P(\mathbf{r}_0 \mid \mathbf{r}, \Delta)$. Since the P_a we get could be the correct behavior insofar as the data tell us, we must rely upon physical arguments to anticipate a dependence upon $\mathbf{r}_0$. To test the usefulness of this particular approximation, we treat the two examples of restricted diffusion which we have already worked out. From Eq. (15) we obtain

$$P_a(\mathbf{r}, \Delta) = [4\pi D(1 - e^{-\beta\Delta})/\beta]^{-\frac{3}{2}} \times \exp[-\beta r^2/4D(1 - e^{-\beta\Delta})]$$

which may be compared with Eq. (14). Note that for small Δ the two expressions give similar results but that for large Δ the expression above predicts twice the spread of probable displacements. From Eq. (18) we obtain

$$P_a(\mathbf{r}, \Delta) = (8\pi a^2 D\Delta)^{-1} \exp(-r_{||}^2/4D\Delta) \times \{[(r_\perp + a)^2]^{\frac{1}{2}} + [(r_\perp - a)^2]^{\frac{1}{2}} - 2(r_\perp^2)^{\frac{1}{2}}\}.$$

When we compare this result with Eq. (17) we see that the behavior parallel to the layer is unchanged and that the rectangular distribution function of width a introduced for the behavior perpendicular to the layer has been replaced by an isosceles triangular distribution with a base of width $2a$. While the relationship between the rectangular distribution, any point of which is a possible starting point, and the triangular distribution, in which one must begin at the center, seems intuitively meaningful, it is not clear how the correct distribution may be recognized and characterized.

DISCUSSION

There are several shortcomings apparent in the use of a pulsed-gradient experiment to unravel the mysteries of a system showing restricted diffusion. Even when the structure of the system is well understood, the differential equations (with boundary conditions) and integrals which must be solved may be formidable. As an investigative tool, the method has an incomplete ability to analyze the expermiental data in terms of an unambiguous structure or behavior. The experimental problem is far from simple.[8,13] Nonetheless, the uses which may be suggested for this experimental technique cover a broad range of classes of systems and many instances occur in which information concerning diffusion over short distances, however incomplete or imperfect, is exceedingly difficult to obtain by other means.

A number of systems may be mentioned as possible subjects for investigation by means of the pulsed gradient spin-echo experiment.[16] A study of solvent diffusion in a macromolecule–solvent system may be expected to reveal something about the environment on the molecular level experienced by the solvent molecules. Woessner's experience in the case of benzene dissolved in rubber substantiates this possibility.[1] Care must be used in selecting systems to be studied since too thorough affinity for the solvent by the macromolecule will make the environment too uniform to reveal restricted diffusion. Colloidal systems offer perhaps a better opportunity to control the dimensions and properties of the restrictions to diffusion, thus making the effects easier to discuss.[1] In a foam, diffusion must take place in the liquid surrounding the gas bubbles. In an emulsion there will be three kinds of diffusion to observe: diffusion within the droplets, diffusion around the droplets, and diffusion of the droplets themselves. A gel will resemble a macromolecule–solvent system. Colloidal particles with a mobile surface-sorbed layer will offer a peculiar type of restricted diffusion. Living cells form a class of colloidal particles which should exhibit restricted diffusion of the substances confined within the cell walls. Examples of anisotropic and/or restricted diffusion

[16] A forthcoming publication by J. E. Tanner and myself will present experimental data from several systems of the types described below. See also: J. E. Tanner, Ph.D. thesis, University of Wisconsin (in preparation).

may be found in various layered systems: Wood and the vermiculites[17,18] are two examples of structures which take up liquids into anisotropic sites, which sites also provide considerable restriction to diffusion. The application of the pulsed-gradient spin-echo experiment to flowing systems may take several forms. When used as a flow meter, the phase shift of the echo indicates the total integrated flow of material between the two gradient pulses. On the other hand, it should be possible to adapt the treatment presented in this paper to interpret the results of the pulsed gradient experiment in a system displaying turbulent flow so as to yield a spectrum of turbulence velocities. An interesting experiment involving both diffusion and flow could be done on a system containing long molecules capable of being oriented by flow. The pulsed-gradient technique could be used to determine the rate of flow as well as the effect of flow rate on the diffusion coefficient, including anisotropic and restrictive effects, resulting from the orientation of the long molecules. Liquid crystals of course provide examples of oriented systems attainable in the liquid state without the system being required to move.

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On the Nonlinear Dielectric Behavior of Desoxyribonucleic Acid Fibers at Low Frequencies

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The dielectric behavior of moist desoxyribonucleic acid fibers at low frequencies has been studied, and is explained phenomenologically. This behavior is nonlinear with respect to the thickness of the sample and to the applied voltage. The experimental results can be reproduced if the conductance of the sample is approximated by a constant term plus a term increasing with the applied voltage. Consequently, at low voltage the behavior appears linear with respect to the voltage, but still depends upon the thickness of the sample; the conductance and capacitance per unit area of electrode are the important quantities. Under this condition (low voltage) a region of absorption has been found, with a critical frequency of 0.014 cps at 25°C and very large apparent dielectric constant ($\epsilon' \approx 10^6$). This behavior is interpreted as being due to the formation of an ionic double layer at the electrodes. The nonlinear phenomenon is attributed to the fact that with increased voltage the electrodes become less blocking.

1. INTRODUCTION

THE dielectric behavior of DNA (desoxyribonucleic acid) fibers has recently attracted attention by an unexpected phenomenon: Polonsky and co-workers[1] have observed low-frequency hysteresis cycles similar to those of ferroelectrices. (See Figs. 2 and 3.) They have subsequently[2] put forward the hypothesis that the phenomenon is due to the movement of ionic charges. Dielectric studies done independently in our respective laboratories in France and the U.S. have confirmed the above hypothesis and allow further explanation for the existence and unusual behavior of the hysteresis cycles that are obtained.

2. EXPERIMENTAL

The electrical arrangement used by us was similar to that of Polonsky *et al.*[1] and is shown in Fig. 1. With this circuit the deflection of the oscilloscope trace along the X axis is proportional to the charging voltage on Sample X, while the Y-axis deflection is normally proportional to the charge transfer but, under certain conditions, may be more complicated (see Appendix). It is commonly used for the detection and measurement of ferroelectricity. In some experiments the capacitor Γ

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