

Spatially-Distributed Pulsed Gradient Spin Echo NMR using Single-Wire Proximity

Paul T. Callaghan¹ and Janez Stepisnik²

¹*Department of Physics, Massey University, Palmerston North, New Zealand*

²*J. Stefan Institute, University of Ljubljana, Ljubljana, Slovenia*

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NMR microimaging may be used to observe the effect of molecular diffusion in the vicinity of a thin wire subjected to current pulses. By this means the pulsed gradient spin echo technique can utilize very large pulsed magnetic field gradients, on the order of 100 T m^{-1} . The quadratic dependence of gradient amplitude on distance from the wire leads to large dynamic range while the distribution of local gradient vectors makes it possible to image anisotropic diffusion. We demonstrate these properties in measurements on polymer solutions and liquid crystals.

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The two principal methods available for the measurement of nuclear spin displacements, inelastic neutron scattering, and pulsed gradient spin echo (PGSE) NMR, are complementary in the distance and time scales to which they are sensitive [1]. However, the lower resolution limit of PGSE ^1H NMR is around 10 nm and nearly an order of magnitude larger than the upper limit of neutron scattering. The PGSE lower limit depends on both the maximum available magnetic field gradient and the degree to which the gradient pulse amplitudes can be accurately matched.

Most methods for producing large pulsed magnetic field gradients rely on the use of a specialized wire array that surrounds the rf coil and produces a linear magnetic field gradient over the sample. When large numbers of turns are used in order to generate large gradients, the resulting inductance tends to limit the rate at which the current may be switched while significant stray magnetic fields result in persistent eddy currents in the surrounding magnet structure. In this Letter we describe a new method of generating very large amplitude gradient pulses. The simplicity of the apparatus required is such as to make the technique accessible to a very large number of potential users. At the heart of the method is the capacity to spatially resolve the sample, depending as it does on the NMR microimaging technique, now routine in a large number of NMR laboratories around the world. Our method utilizes the divergence in gradient strength that occurs in the vicinity of a current-carrying wire. Rather than surrounding our sample with an external gradient coil, we have inserted a current carrying wire in the sample itself.

The results reported here are novel in a number of respects. First, we are able to use diffusive attenuation to image the magnitude of the local gradient in the absolute magnetic field. Second, we are able to demonstrate that the available magnetic field gradients are in excess of those currently accessible in pulsed experiments, and that the wide variation in gradient amplitude across the image plane confers an enormous dynamic range on the experiment. Finally we are able to utilize the variation

in local gradient directions near the wire to observe anisotropic diffusion in a single two-dimensional image.

In a PGSE NMR experiment comprising two narrow gradient pulses of amplitude g and duration δ , and separation Δ , the echo amplitude E is given by the ensemble average $\exp(iqZ)$ where q is $\gamma g \delta$, Z represents the translational displacement of the nuclear spins over the time Δ , and γ is the nuclear (in our case, proton) gyromagnetic ratio. In the case of unrestricted molecular self-diffusion, this average returns the result [2]

$$E(q) = \exp(-q^2 D \Delta_r), \quad (1)$$

where D is the molecular self-diffusion coefficient and Δ_r is the reduced diffusion time, $\Delta_r = \Delta - \delta/3$. Notice that the nuclear displacement scale Z , to which the method is sensitive, is on the order of q^{-1} and therefore depends on both the gradient amplitude and the gradient pulse duration. The available time for the pulse is limited by nuclear spin relaxation. For example, with typical polymer proton relaxation times on the order of 10 ms, a gradient amplitude of 10 T m^{-1} implies $q^{-1} \sim 30 \text{ nm}$.

In considering PGSE behavior in the vicinity of a single wire, we are required to address the issue of a strongly inhomogeneous magnetic field $\mathbf{B}(\mathbf{r})$. Since the method depends on the absolute Larmor frequency, the relevant local gradient is $\text{grad}|\mathbf{B}|$ [3]. For a long straight wire oriented transverse to the polarizing field \mathbf{B}_0 , this is given by

$$\mathbf{g} = \frac{\mu_0 I}{2\pi(x^2 + y^2)^{3/2}(a^2 - 2ax + x^2 + y^2)^{1/2}} \times \{(x^2 - y^2 - ax)\mathbf{i} + (2xy - ay)\mathbf{j}\}, \quad (2)$$

where a is $(\mu_0 I / 2\pi B_0)$ and \mathbf{i} and \mathbf{j} are unit vectors in the normal plane where \mathbf{j} refers to the direction of the polarizing field. It should be noted that for our experiments in a 7 T polarizing field, the largest current used is 8 A and consequently $a \approx 0.2 \mu\text{m}$. Given that we shall be concerned with distances in excess of $10 \mu\text{m}$, the equation simplifies to

$$\mathbf{g} = \frac{\mu_0 I}{2\pi(x^2 + y^2)^2} \{(x^2 - y^2)\mathbf{i} + 2xy\mathbf{j}\}. \quad (3)$$

Figure 1 shows the radiating pattern of local gradient vectors along with the equigradient contours. These contours are centered on the wire and exhibit an inverse square relation $|\mathbf{g}| = \mu_0 I / 2\pi r^2$ where $r = (x^2 + y^2)^{1/2}$.

Because of the quadratic dependence on q in the exponent in Eq. (1), the echo attenuation for an isotropically diffusing fluid in the vicinity of the wire exhibits a severe *exponential inverse fourth power* dependence on the distance r from the wire center. This point serves to dramatically emphasize the enormous dynamic range available across the image plane transverse to the wire. It means, in effect, that one can use the technique to measure molecular diffusion coefficients different by many orders of magnitude without the need to greatly vary the amplitude or duration of the current pulses. As a result of the severe dependence on r of the exponent $q^2 D \Delta$, the image amplitude for a given molecular component is expected

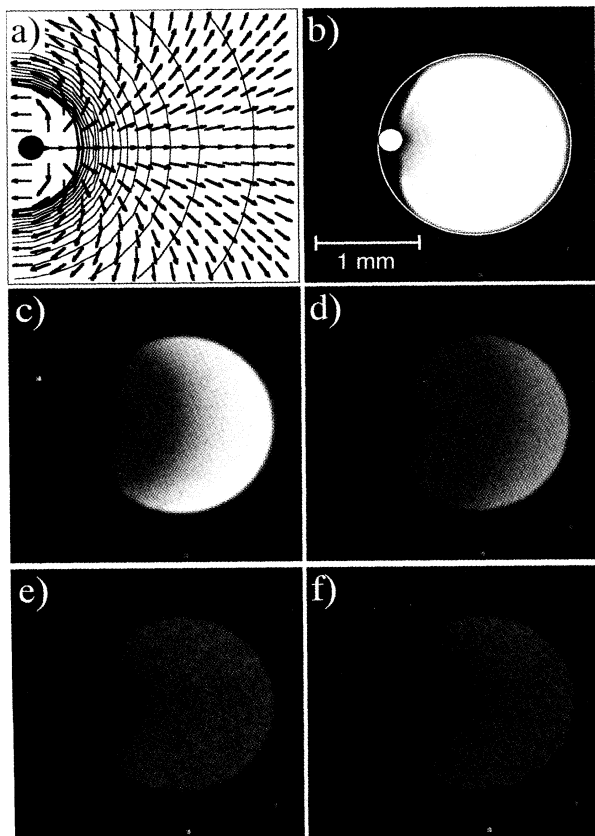


FIG. 1. (a) Distribution of gradient vectors superposed on equigradient contours. Note that the polarizing field is in the vertical direction and normal to the wire. (b) to (f) show NMR images (FOV 3 mm) of the solution of PEO in water obtained using the PGSE sequence with $\Delta = 20$ ms. In (b) ($I = 0$) the white superposed circles show the inner glass capillary wall and the wire position. The black region near the wire is due to the epoxy. Note the crescent of the water diffusion boundary which expands from (c) ($I = 1.2$ A, $\delta = 2$ ms) to (d) ($I = 2.4$ A, $\delta = 2$ ms), while in (e) ($I = 2.0$ A, $\delta = 9.6$ ms) and (f) ($I = 7.7$ A, $\delta = 10.0$ ms) the polymer diffusion boundary develops and expands.

to exhibit a constant plateau when $q^2 D \Delta_r < 1$, which drops quite suddenly to zero over the space of a few pixels, where $q^2 D \Delta_r > 1$. The position of this rather sharp boundary in the image can then be used to determine the value of D .

In order to illustrate these points we have carried out a proton NMR experiment at an ambient temperature of 25 °C using, as a sample, a solution of 5% 1.0×10^6 amu poly(ethylene oxide) in water. While the water diffusion coefficient is $2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, the polymer diffusion is known to be [4] some 4 orders of magnitude slower. The solution was placed in a glass capillary tube of 1.6 mm inner diameter. Prior to sample insertion a copper wire filament of 0.2 mm diameter had been attached to the inner surface of the glass using 5 min epoxy. Our experiment was performed using a Bruker AMX300 NMR spectrometer with microimaging attachment in which the horizontal 3 mm rf solenoid coil was used to hold the capillary.

Figures 1(b)–1(f) show a succession of spin echo amplitude images taken at successively increased values of the product $I\delta$ where I is the amplitude of the current pulse. At zero current in the wire the image exhibits a uniform amplitude and the dark region on the left-hand edge shows quite clearly the outline of the circular wire cross section along with the meniscus of the epoxy resin used to secure the wire to the inner wall of the glass capillary. At the smallest (nonzero) value of $I\delta$ ($I = 1.4$ A, $\delta = 2$ ms), shown in Fig. 1(c), the attenuation boundary for the water molecules is clearly apparent at a distance of about 1 mm from the wire center. As $I\delta$ is increased, this boundary, as expected, moves further from the wire. On each side of the water boundary the plateau regions are clearly delineated. On the distant side the constant amplitude is due to the total contribution of water and polymer protons while on the near side the water signal has vanished, leaving a constant polymer proton plateau. By subtracting this plateau we obtain the water proton echo attenuation plot shown in Fig. 2. Here the inverse fourth power dependence of $q^2 D \Delta_r$ on pixel displacement is clearly demonstrated, and from the slope, which measures the effective rate of incline at the attenuation boundary, we are able to ascertain the diffusion coefficient with an accuracy of a few percent.

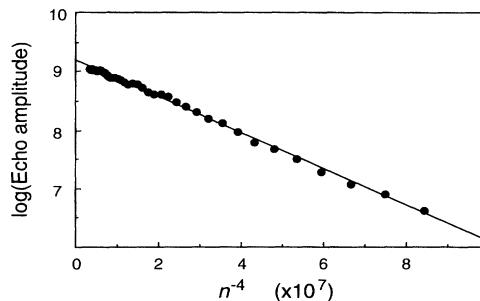


FIG. 2. Echo attenuation plot obtained from a diametrical slice across the image shown in Fig. 1(c).

In the low current images the local magnetic field gradient is sufficient to dephase the polymer proton spin echo only in the few pixels very close to the wire. However, as $I\delta$ is increased further, this inner polymer attenuation boundary recedes from the wire and moves clearly out into the capillary space. In the final image in which the current is 7 A, the gradient ten pixels from the wire/solution interface is 14 T m^{-1} while the gradient two pixels from the interface is 70 T m^{-1} . The remarkable size of these gradients serves to illustrate the convenience and power of the method. For example, it is possible to accurately measure a diffusion coefficient by simply locating the position of the sharply defined plateau boundary, a procedure that is aided by the circular shape of the attenuation ring. This ring further serves to locate the wire center.

It may be argued that by immersing the wire on the fluid to be examined, we risk local heating effects that will perturb the diffusion measurements. Our calculations show that a copper wire of diameter 0.2 mm with two 10 ms current pulses of 10 A will deposit 25 mJ per mm of wire length. Allowing for the thermal conductivity of the water and making the rather crude assumption of radial heat flow, we estimate that this deposition would result in a temperature rise of around 1°C within a $50 \mu\text{m}$ thick layer around the wire surface. This is not expected to cause a problem in the measurements. However, if this localized heating is to be avoided, or if one is using a liquid which may react with the epoxy wire support, it is possible to utilize a wire glued on the outside surface of the capillary. For thin-walled glass of around 0.1 mm thickness, the loss in available gradient would be minimal. Such an experiment is shown in Fig. 3 where a 10% solution of 1.75×10^6 amu polystyrene in CCl_4 is placed in a 1.0 mm outside diameter (o.d.) [0.8 mm inside diameter (i.d.)] glass capillary on which a wire had been glued to the external surface ($I = 4.0 \text{ A}$, $\delta = 12 \text{ ms}$). The location of the diffusion boundary at $270 \mu\text{m}$ from the wire center (local gradient 11 T m^{-1}) leads to a diffusion coefficient of $5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, consistent with the expected value [5].

A further artifact to which the method might be susceptible concerns wire or sample movement caused by the interaction of the current and the polarizing field. We have found that this force caused no difficulties, provided that the capillary tube was inserted tightly into the rf coil using Teflon tape. Motion artifacts were observed only when the capillary was sufficiently loose to be manually displaced.

On examining the images shown in Fig. 1, it is quite clear that the attenuation boundaries for both the water and the polymer do indeed closely approximate circles centered on the wire, thus clearly indicating that the diffusion is indeed isotropic. The use of this two-dimensional information from the spatially-distributed PGSE experiment serves to illustrate just how potentially useful this technique can be in revealing diffusion anisotropy when the echo attenuation depends on the local gradient $\mathbf{g}(\mathbf{r})$

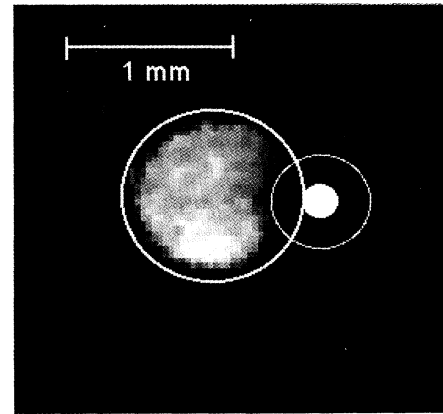


FIG. 3. Image of the polymer proton NMR signal in a solution of 10% 1.75×10^6 amu polystyrene in CCl_4 for which $I = 4.0 \text{ A}$, $\delta = 12 \text{ ms}$, and $\Delta = 15 \text{ ms}$. The superposed white circles show the outer wall of the 1.0 mm o.d. glass capillary, the externally attached wire and the circle defining the e^{-1} attenuation point on the polymer image.

and the self-diffusion tensor $\mathbf{D}(\mathbf{r})$ as

$$E(\mathbf{r}) = \exp\{-[\gamma^2 \delta^2 \mathbf{g}(\mathbf{r}) \cdot \mathbf{D}(\mathbf{r}) \cdot \mathbf{g}(\mathbf{r}) \Delta_r]\}. \quad (4)$$

To emphasize this point we have investigated the shape of the boundary image in the case of a fluid where the diffusion is clearly anisotropic. The system we have chosen is the lamellar phase of the lyotropic liquid crystal, Aerosol OT [bis(2-ethylhexyl) sodium sulphosuccinate] (50/50 w/w with water). For such a system water diffusion parallel to the lamellar bilayers is known to be more than an order of magnitude faster than diffusion in the normal direction [6]. It is also known that, in contact with a glass surface, the bilayers will assume a preferential orientation parallel to the interface. As a consequence, when placed in the cylindrical capillary, we would expect the system to organize in a concentric structure akin to the schematic diagram shown in Fig. 4(a). While some disorder must exist at the capillary center, in the perimeter region the system may be sufficiently symmetrically organized that the diffusion tensor can be quite simply described in a cylindrical polar reference frame as comprising free diffusion in the azimuthal direction and strongly restricted diffusion in the radial direction. The result of our calculation based on the line gradient distribution shown in Fig. 1 and the diffusional anisotropy shown in Fig. 4(a) is the attenuation boundary of Fig. 4(b). This “butterfly wing” shape is precisely what one would expect intuitively since the boundary will extend farthest when the local gradient vectors are predominantly azimuthal in orientation and least when those vectors are directed along a radius. This latter direction is the path directly horizontally out from the wire.

Figure 4(c) shows the result of our experiment, again performed using a 1.6 mm i.d. glass capillary. Here the current pulse amplitude is 5.2 A and the gradient pulse duration is 1.0 ms. While the image is somewhat

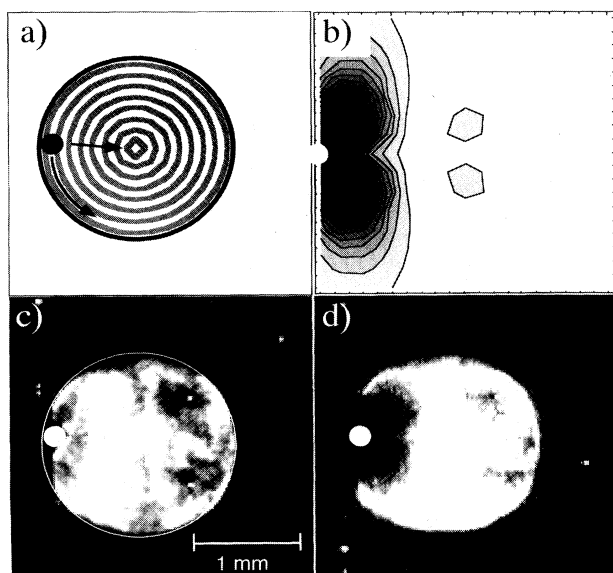


FIG. 4. (a) Schematic representation of the lamellar phase of AOT/water in which the lamellae are presumed to be concentric cylinders aligned parallel to the glass surface. (b) Calculated echo amplitude image based on a diffusion anisotropy (D_{\parallel}/D_{\perp}) of 20. (c) and (d) are images obtained with $I = 0$ and with $I = 5.6$ A, $\delta = 1$ ms, and $\Delta = 3.6$ ms, respectively.

distorted and nonuniform (probably due to local susceptibility artifacts and uneven interlamellar spacing), the “butterfly wing” attenuation boundary is obvious, thus confirming our hypothesis concerning the concentric lamellar phase organization in this sample.

The potential materials science applications of spatially-distributed pulsed gradient spin echo NMR using single-wire proximity are numerous. As has been already indicated, the very small inductances of the gradient “coil” make rapid pulse switching entirely feasible, thus providing access to the submillisecond regime. While any shortening of pulse duration values requires a corresponding increase in gradient amplitude if the same sensitivity to molecular displacement is to be preserved, this increase is provided by the quadratic rise in gradient amplitude in the vicinity of the wire. As with all PGSE experiments involving pulse switching using an external current supply, the method is vulnerable to pulse amplitude mismatch caused by current noise or ripple. It is also susceptible to phase artifacts caused by sample movement. However, it has been noted in an earlier article by one of us [7] that pulse mismatch and sample movement artifacts can be completely removed provided that a small read gradient is used and signal averaging is performed in the frequency domain subsequent to a modulus Fourier transform on each individual echo. One of the very nice features of spatially-distributed pulsed gradient spin echo NMR is that it lends itself quite naturally to such averaging since the echo-centering read gradient is already in place as an integral part of the method.

It should be remarked that the absolute magnitude of the pulsed gradients reported here using the single-wire method is comparable with the steady gradients available in the fringe field of superconducting magnets. Spin echo NMR diffusion experiments performed in such stray fields have proven highly valuable in the measurement of very slow diffusion [8]. Our approach represents an alternative strategy in which it is possible to avoid some of the disadvantages of the fringe field method, such as the need to operate at reduced Larmor frequency and the inability to perform spectroscopic studies.

Finally, we note that the apparatus necessary to perform spatially-distributed pulsed gradient spin echo NMR is extremely simple provided that one has the necessary, but readily available, microimaging attachment to the spectrometer. The experiments reported here illustrate clearly the importance of high spatial resolution in the image plane. Normally, when imaging small molecules such as water, the ultimate limit to imaging resolution is fixed by molecular self-diffusion over distances on the order of the pixel dimension. It has not escaped our notice that in the case of large gradient PGSE NMR, where very slow diffusion is to be investigated, this limit is drastically reduced. As a consequence we expect that the pixel resolution of $23 \mu\text{m}$ used in the present study could be considerably improved. This being the case we would estimate that the available *useful* gradient could be much higher than that reported here. Indeed we suggest that gradients well in excess of 100 T m^{-1} should be feasible, making it possible to measure molecular displacements, over the time duration between the gradient pulses, smaller than 10 nm. Such resolution would bridge the gap between PGSE NMR and inelastic neutron scattering in investigations of molecular dynamics in condensed matter.

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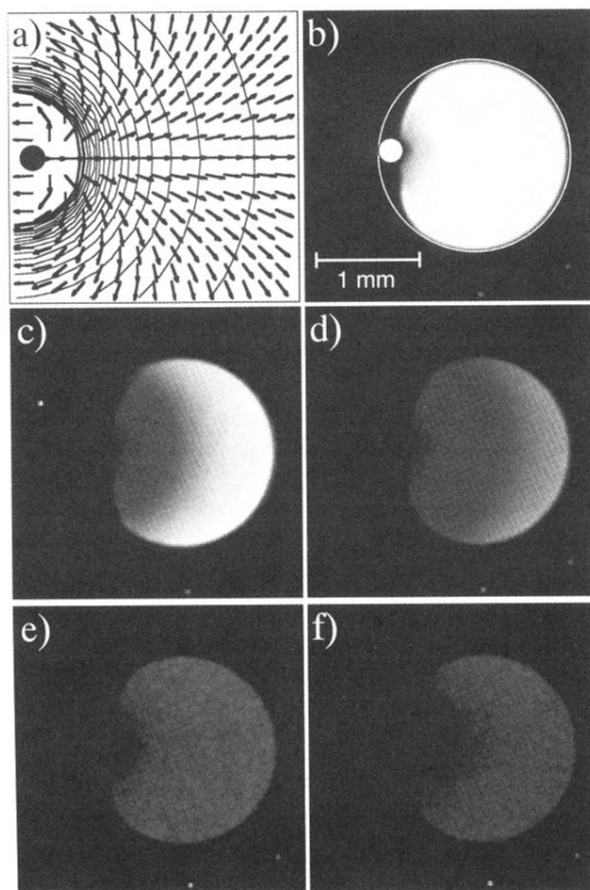


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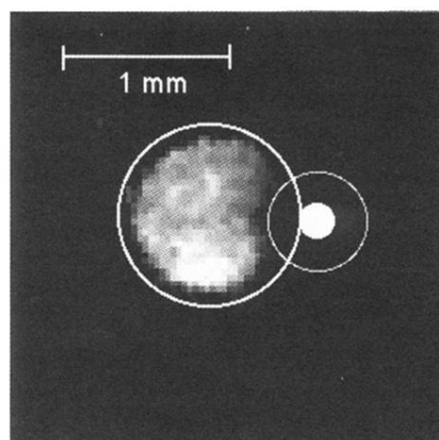


FIG. 3. Image of the polymer proton NMR signal in a solution of 10% 1.75×10^6 amu polystyrene in CCl_4 for which $I = 4.0$ A, $\delta = 12$ ms, and $\Delta = 15$ ms. The superposed white circles show the outer wall of the 1.0 mm o.d. glass capillary, the externally attached wire and the circle defining the e^{-1} attenuation point on the polymer image.

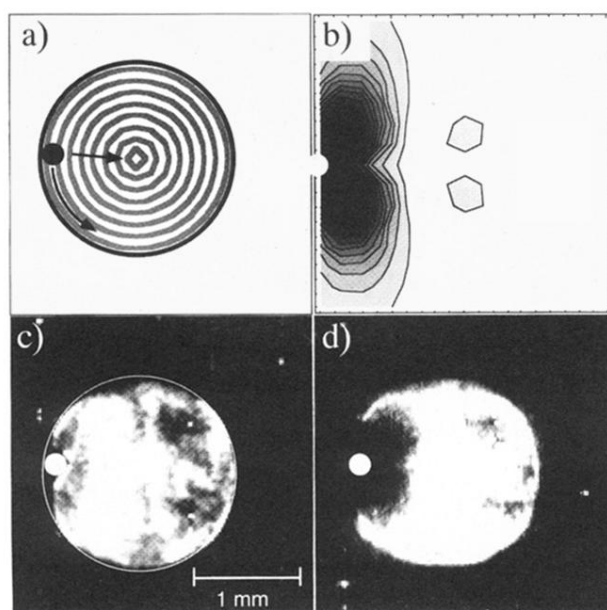


FIG. 4. (a) Schematic representation of the lamellar phase of AOT/water in which the lamellae are presumed to be concentric cylinders aligned parallel to the glass surface. (b) Calculated echo amplitude image based on a diffusion anisotropy (D_{\parallel}/D_{\perp}) of 20. (c) and (d) are images obtained with $I = 0$ and with $I = 5.6$ A, $\delta = 1$ ms, and $\Delta = 3.6$ ms, respectively.