Probing Porous Media with Gas Diffusion NMR

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We show that gas diffusion nuclear magnetic resonance (GD-NMR) provides a powerful technique for probing the structure of porous media. In random packs of glass beads, using both laser-polarized and thermally polarized xenon gas, we find that GD-NMR can accurately measure the pore space surface-area–to–volume ratio, S/V_p, and the tortuosity, α (the latter quantity being directly related to the system's transport properties). We also show that GD-NMR provides a good measure of the tortuosity of sandstone and complex carbonate rocks.

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In this paper we demonstrate a powerful new probe of porous media, NMR measurements of the time-dependent diffusion of imbibed gas. Porous media are ubiquitous in nature. Examples include granular materials, foams, ceramics, reservoir rocks, and animal lungs and sinuses. Their structure is relevant to a wide range of scientific, technological, and medical problems. For example, knowledge of the transport properties of fluids in subsurface rocks is important for the monitoring of contaminant percolation and for hydrocarbon extraction. In connection with the latter, we note the growing importance of gas reserves from both a commercial and environmental perspective. Similarly, monitoring the evolution of porous materials subjected to large thermal or mechanical stress may help characterize the dynamics of cracking and failure. Also, noninvasive measures of the lung's surface-area–to–volume ratio could advance our understanding of normal physiology as well as disease diagnosis. Gas diffusion NMR (GD-NMR) should be applicable to these and many other situations, allowing noninvasive determinations of the structure of porous media.

NMR measurements of the diffusion of *liquids* imbibed in porous media is a well-understood technique that provides important information on sample structure for lengths below $\sim 50\ \mu\text{m}$ [1–4]. This upper limit is set by (i) the relatively slow molecular diffusion in liquids compared to the inherent decay of their spin polarization (i.e., T_1 decay), and (ii) enhanced relaxation of spin polarization at pore boundaries. However, many porous systems have structure on length scales greater than $\sim 50\ \mu\text{m}$. For such systems, imbibed-liquid NMR may accurately measure the porosity and pore surface-area–to–volume ratio (S/V_p), but is not able to determine physical properties associated with the interconnectivity and tortuosity [5] of the pore space [6,7]. Further, imbibed-liquid NMR is inherently incompatible with nonsolid porous systems, such as wet foams, and with structures in living subjects (e.g., lungs and sinuses).

By contrast, NMR techniques based on an imbibed noble gas take advantage of three physical effects: (i) gas diffusion coefficients are typically orders of magnitude larger than those of liquids, (ii) the weak interaction of noble gas atoms with pore surfaces leads to long NMR lifetimes, and (iii) noble gases are chemically inert and biologically compatible. In addition, gases have an important experimental advantage, the ability to alter the bulk diffusion coefficient by varying the pressure or by introducing buffer gases. This significantly expands the range of distances that can be probed in comparison to liquid NMR, where bulk diffusion coefficients are more difficult to manipulate. Thus, NMR measurements of restricted diffusion of noble gases have great potential as a multipore probe of porous media.

Gas-phase NMR has received considerable attention following the development of laser-based optical pumping techniques to produce large nuclear spin polarizations ($\sim 10\%$) in dense samples of the spin-$\frac{1}{2}$ noble gases, ^{129}Xe and ^{3}He [8]. Recent publications have addressed the measurement of *time-independent* noble gas diffusion coefficients while accounting for the nonrenewable spin polarization provided by laser-polarization techniques [9–12]. We recently demonstrated experimental techniques for measuring *time-dependent* gas diffusion in a restricted environment [13]. In this paper we show that NMR diffusion measurements of laser-polarized and thermally polarized ^{129}Xe gas imbibed in bead packs and rocks can probe distances well beyond a pore diameter, and that such measurements are directly related to the system's transport properties.

NMR measurements of the time-dependent diffusion coefficient of a fluid typically employ variants of the pulsed gradient spin echo (PGSE) protocol developed by Stejskal and Tanner [14]. A magnetic field gradient pulse is applied to twist the phase of the transverse magnetization, effectively encoding spatial information with a magnetization phase modulation. A second gradient pulse, occurring at time t after the first pulse, unwinds the applied phase modulation, thereby creating a spin echo and a detectable NMR signal. (This diffusion time t is sometimes referred to as Δ in the literature [1,13,14].) The key to the PGSE technique is the *differential* spatial encoding provided by the two magnetic field gradient pulses. Only spins that have not moved during the time t receive exactly equal and opposite phase modulations. Spins that have undergone diffusion during the interval t are out of phase to some degree with the spin ensemble average, and contribute less to the detected spin echo signal. The larger the fluid's effective diffusion coefficient $D(t)$, the greater the diffusion distance $d \sim \sqrt{D(t)t}$ for a given t. [$D(t) \equiv \langle[\mathbf{r}(t) - \mathbf{r}(0)]^2\rangle/(6t)$, where $\mathbf{r}(0)$ and $\mathbf{r}(t)$ denote a given spin's position at the time of the first and second gradient pulses, respectively, and the angle brackets imply an ensemble average over all spins in the system.] If diffusion is restricted, as in porous media, then there will be less diffusive attenuation of the NMR signal for a given t. Thus, for t much less than the time for a spin to diffuse across a pore, fluid diffusion coefficients close to those of the bulk fluid are measured, whereas for longer t, the observed diffusion coefficient decreases as the fluid spins are increasingly restricted by the pore boundaries. With such measurements of $D(t)$, the structure of porous media can be probed [15].

For small t, the fraction of fluid spins whose motion is restricted by pore boundaries is $\sim(S/V_p)\sqrt{D_0 t}$, where S/V_p is the pore surface-area–to–volume ratio. Specifically, Mitra *et al.* have shown [15,16]

$$D(t)/D_0 = 1 - \frac{4}{9\sqrt{\pi}}\frac{S}{V_p}\sqrt{D_0 t} + \mathcal{O}(D_0 t). \tag{1}$$

This relation has been verified experimentally with NMR of liquids imbibed in a variety of porous media [3]. If spin relaxation at the pore boundary can be neglected, then, for large t, $D(t)$ reaches an asymptotic limit defined by the Einstein relation [17],

$$D(t)/D_0 \rightarrow 1/\alpha\,, \tag{2}$$

where α is the tortuosity of the porous medium [5]. In random bead packs, $1/\alpha \approx \sqrt{\phi}$, where ϕ is the porosity [17].

As a first demonstration of GD-NMR as a probe of porous media, we used thermally polarized xenon gas imbibed into a well-understood model system, dense random packings of spherical glass beads. ("Thermally polarized" refers to the spin polarization resulting from the equilibrium energy state population difference in an applied magnetic field, as defined by the Boltzmann condition. For xenon at room temperature, this equates to $\sim 4.6 \times 10^{-6}$ tesla^{-1}.) Cylindrical glass cells of volume ~ 50 cm^3 held the bead packs. Each cell contained beads of a single size, with bead diameters in different cells ranging from 100 μm to 4 mm; the corresponding average pore sizes ranged from ~ 20 μm to 1 mm. Typically, three bars of xenon (isotopically enriched to 90% ^{129}Xe) and two bars of oxygen at room temperature were imbibed in the bead packs. (Paramagnetic oxygen was included to reduce the ^{129}Xe T_1 to ~ 1 s, thereby enabling efficient signal averaging of the low NMR signal provided by thermally polarized ^{129}Xe gas.) GD-NMR experiments were performed at 4.7 T on a GE Omega/CSI spectrometer, operating at 55.348 MHz for ^{129}Xe, and providing applied magnetic field gradients up to 7 G/cm in strength.

Figure 1 shows typical results for time-dependent diffusion measurements of thermally polarized ^{129}Xe gas imbibed into random bead packs, acquired with a stimulated echo variation of the PGSE technique using bipolar gradient pulses [18,19]. Data for the larger beads (and hence larger pores) agree well with theoretical limits for both short and long diffusion times. For the smaller beads, however, there is systematic disagreement between experiment and theory for short diffusion times: the measurements deviate toward larger values. This deviation likely results from xenon atoms diffusing across a significant fraction of a pore diameter during the finite time it takes to apply the diffusion-encoding magnetic field gradient pulse—a breakdown of the "narrow pulse approximation" [20]. For example, taking the measured free gas diffusion coefficient, D_0, for the xenon-oxygen mixture as 1.36×10^{-6} m^2 s^{-1} [13], the characteristic diffusion distance during the Omega spectrometer's minimum gradient pulse time of 750 μs is approximately 32 μm. Candidates for correcting the small-pore–small-t breakdown of GD-NMR include (i) greater gas pressure, (ii) a large cross-section buffer gas, (iii) more rapid gradient pulses, and (iv) a more detailed theoretical analysis to allow S/V_p to be determined when the narrow pulse approximation is not satisfied [21].

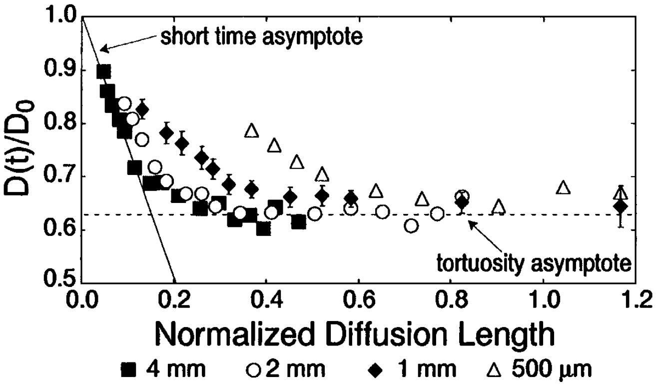

FIG. 1. Time-dependent diffusion measurements for thermally polarized xenon gas imbibed in randomly packed spherical glass beads. Each sample contains beads of a uniform diameter b, as indicated in the legend. Data is shown as the time-dependent diffusion coefficient normalized to the free gas diffusion coefficient, $D(t)/D_0$, as a function of the free gas diffusion length in the time t normalized to the bead diameter, $\sqrt{D_0 t}/b$. Error bars are shown for the 1 mm beads and are similar for the other measurements. The calculated limits at short time (surface-area–to–volume ratio, S/V_p) and long time (tortuosity, α) are shown by the solid and dashed lines, respectively. For dense spherical bead packs, $\phi = 0.39$, $1/\alpha \approx \sqrt{\phi} = 0.63$, and $S/V_p = 6(1 - \phi)/(\phi b) = 9.38/b$.

We next demonstrated GD-NMR in glass bead packs using laser-polarized ^{129}Xe gas. Laser polarization of the xenon gas was performed in the fringe field of the 4.7 T Omega NMR magnet using the spin-exchange optical pumping technique [8]. The polarized gas was then admitted to an evacuated sample cell containing a bead pack. Because of the finite, nonrenewable magnetization of laser-polarized samples, we employed an experimental system that delivered a new shot of laser-polarized xenon gas into the bead pack for each diffusion time, t, and gradient setting. Figure 2 shows the results of a time-dependent diffusion measurement for 3 bar of laser-polarized xenon gas (with a natural isotopic abundance of ~27% ^{129}Xe) imbibed into a dense, random pack of 3 mm beads. Essentially identical results were obtained using thermally polarized ^{129}Xe gas. With an automated system to pump out and replenish the laser-polarized gas, a full range of ^{129}Xe $D(t)$ NMR data can be obtained much more rapidly (a few minutes) than the several hours required for a thermally polarized ^{129}Xe measurement.

Having successfully used xenon GD-NMR to probe multiple pore distances in model porous media, we applied this new technique to quarried rocks: samples of Fontainebleau, a clay-free sandstone, and Indiana limestone, a carbonate rock with complex pore structure [6]. In rocks with typical pore sizes greater than tens of μm, liquid diffusion NMR is unable to probe multipore length scales required to reach the tortuosity limit [6,7] because of slow liquid diffusion and spin depolarization at pore surfaces. This limitation can be seen in the imbibed-water diffusion data shown in Fig. 3. For the present experiments, we evacuated cylindrical rock cores (3.8 cm diameter, 10.2 cm length) held in tightly fitting plastic cells, and filled the pore space with thermally polarized xenon gas isotopically enriched to 90% ^{129}Xe. Three and four bars of xenon gas at room temperature were used for the sandstone and carbonate rocks, respectively. Surface interactions inside the rock pores reduced the measured ^{129}Xe T_1 to ~4 s without added oxygen, while the xenon gas in the remaining free regions around the rock core exhibited a $T_1 \sim 15-40$ s. This "free" gas was made essentially invisible in the GD-NMR experiment, either by using a fast repetition rate during signal averaging, or by differential T_1 recovery of the gas in the rock pores following inversion of all ^{129}Xe magnetization in the sample cell.

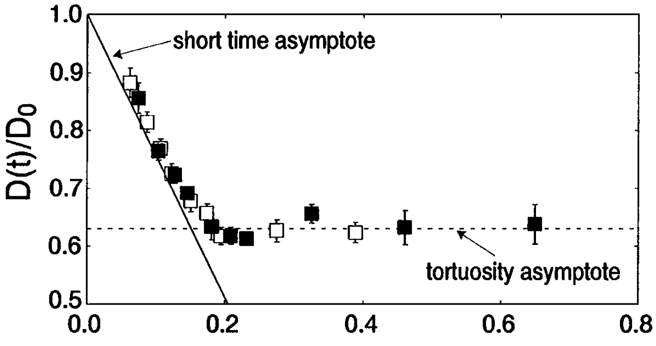

FIG. 2. Comparison of time-dependent diffusion measurement for laser-polarized (filled squares) and thermally polarized (open squares) xenon gas imbibed in randomly packed 3 mm glass beads.

We again used the stimulated echo technique to measure time-dependent diffusion of the imbibed ^{129}Xe gas for t values between 25 ms and 2 s, corresponding to free gas diffusion distances between ~0.2 and 2 mm. The resulting GD-NMR data for Fontainebleau sandstone and Indiana limestone are shown in Fig. 3. The quartz grains in the Fontainebleau sample are approximately 200 μm in diameter [6] and the distribution of pore sizes is very narrow, centered at ~50 μm. As shown in Fig. 3a, the long-time tortuosity limit, inferred from electrical conductivity to be 0.30, is not reached with water diffusion NMR, but is easily reached with xenon GD-NMR. The second rock,

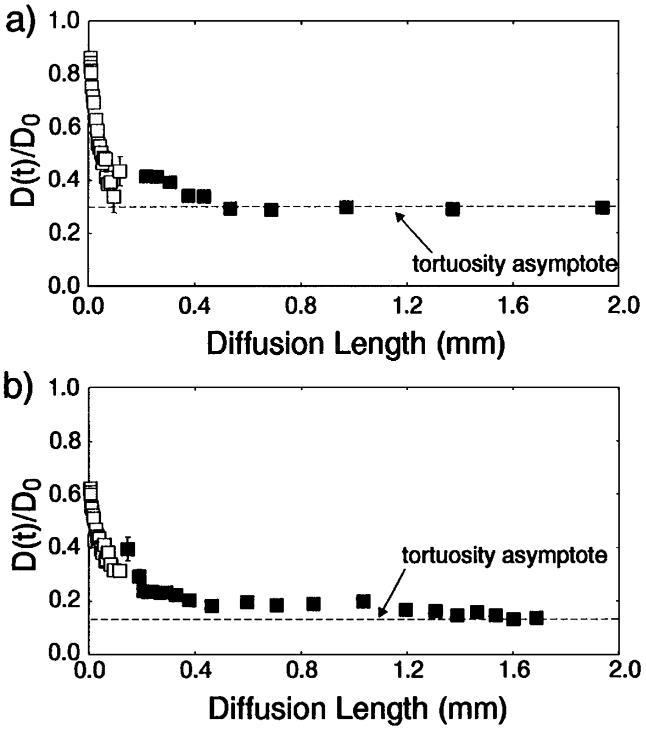

FIG. 3. Time-dependent diffusion measurements for thermally polarized xenon gas (filled squares) and water (open squares) (from Ref. [6]) in sedimentary rocks. The gas and water experiments are complimentary, extending over a diffusion distance of more than 3 orders of magnitude. Only error bars exceeding the size of the data point are shown. (a) In Fontainebleau sandstone the observed inverse tortuosity asymptote from xenon GD-NMR is 0.29 ± 0.01, in excellent agreement with that measured by electrical conductivity of 0.30 ± 0.01 [6]. (b) In Indiana limestone the observed inverse tortuosity asymptote from xenon GD-NMR is 0.13 ± 0.01, again in excellent agreement with that measured by the electrical conductivity of 0.13 ± 0.01 [6].

Indiana limestone, has a much more complex pore structure, with a wide pore-size distribution stretching over roughly 3 orders of magnitude, up to ~1 mm. The inverse tortuosity, derived from electrical conductivity measurements, is 0.13 [6]. As can be seen in Fig. 3b, the water diffusion NMR data drops rapidly for small t, due to the small length scales present in this rock. However, the tortuosity limit cannot be reached with water NMR, because the molecules do not diffuse far enough to probe the longer length scales characterizing the connected pore space. In contrast, these longer length scales are probed successfully with GD-NMR. This is demonstrated in Fig. 3b, where the measured $D(t)$ reaches the tortuosity limit once the free diffusion length exceeds 1.6 mm. The observed $D(t)$ plateaus in the xenon GD-NMR data indicate that the pore space has structure up to ~2 mm. For greater lengths, the rock is apparently homogeneous, in agreement with thin section images. As with the sandstone, there is excellent agreement between the electrical conductivity and gas diffusion NMR determinations of tortuosity. Note that the xenon GD-NMR measurements for small t in both rock samples exhibit systematic deviations to higher values, presumably because of a breakdown of the narrow pulse approximation [20], as discussed above.

In conclusion, we demonstrated that gas diffusion NMR is a powerful new probe of porous media. We used this new technique as follows: (i) to determine the tortuosity and pore surface-area–to–volume ratio (S/V_p) of model porous systems (random bead packs), and (ii) to measure the tortuosity of Fontainebleau sandstone and Indiana limestone rock samples. Tortuosity is an important, long distance property of porous media directly related to the medium's average pore connectivity and transport properties [5]. NMR techniques employing imbibed liquids cannot probe the structure of many porous media of interest over multipore length scales ($\gtrsim 50\ \mu$m) because of slow liquid diffusion and rapid spin relaxation on surfaces at pore boundaries. The use of GD-NMR solves these problems, and is also suited to porous systems incompatible with imbibed liquids, e.g., wet foams and biological systems such as lungs and sinuses. Finally, the use of laser-polarized noble gas allows much more rapid and sensitive GD-NMR measurements.

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