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Diffusion in porous materials as probed by pulsed gradient NMR measurements

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Abstract

Due to recent activity involving diffusion measurements using pulsed gradient spin echo techniques, both experimental and theoretical, we now have a better understanding of diffusion of fluid molecules in a large class of natural and artificial porous media. At short times, the restrictions cause deviations from free diffusion that depend only on local properties of the pore–grain interface. This allows quantities such as the time-dependent diffusion coefficient and the return to the origin probability to be calculated exactly, and these results have been experimentally verified. At longer times, diffraction-like effects are observed in the measured momentum-space diffusion propagator, which can be understood in model systems. In general, it is better understood how diffusion measurements may be used to probe the microgeometry of porous media.

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1. Introduction

The measurement of the diffusive motion of fluid molecules in a porous medium is of interest in a variety of contexts. Such measurements yield information relevant to fluid transport through the medium. In addition, measurements pertaining to diffusion contain information about the microgeometry of the porous medium, and it is of interest to consider the *inverse problem* of extracting information about the microscopic structure of the porous medium from diffusion-related measurements.

An important probe for the diffusive motion of fluid molecules is provided by pulsed gradient spin echo (PGSE) NMR measurements [1,2]. This technique has historically been used to obtain the bulk diffusion coefficient of fluids. More recently, measurements performed on fluids contained in porous media, have been shown to contain information about the microscopic structure of porous media [3,4]. In several experimental efforts,

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PGSE measurements have been performed on water or hydrocarbons in sedimentary rocks or artificial analogs such as randomly packed glass or polystyrene spheres [5–7]. The interest here stems in part from the possibility that such measurements will yield information about the transport of hydrocarbons through porous rocks, or about the microgeometry. NMR diffusion measurements have also generated considerable interest in the case of brain tissue [8], which constitutes a biological porous medium. In this case, the interest stems from the rapid reduction of the effective diffusion coefficient of water protons observed in the brain following ischemia i.e. cerebrovascular stroke [9].

The spin echo amplitude obtained in a PGSE measurement can be most easily understood in terms of a Green's function or propagator [10] of a diffusion equation in the pore space which satisfies appropriate boundary conditions. The PGSE amplitude corresponds to a spatial Fourier transform of this propagator. Quantities of particular interest, for which precise definitions are provided later, are (a) the time-dependent diffusion coefficient, (b) the return to the origin (RTO) probability as a function of time, and (c) the momentum dependence of the diffusion propagator. In this paper, theoretical results involving these quantities are summarised. These results, along with experimental measurements, have yielded some insights into diffusive transport in porous sedimentary rocks, as well as biological tissues, which are also discussed.

2. PGSE measurements and the diffusion propagator

Under ideal circumstances [7], the PFG amplitude $M(\mathbf{k}, t)$ can be expressed in terms of an appropriate diffusion propagator $G(\mathbf{r}, \mathbf{r}', t)$ of fluid molecules in the relevant geometry [10]:

$$M(\mathbf{k}, t) = \int e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} G(\mathbf{r}, \mathbf{r}', t) \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}' . \quad (1)$$

Here $G(\mathbf{r}, \mathbf{r}', t) d\mathbf{r} d\mathbf{r}'$ is the probability that a diffusing spin initially in a small volume $d\mathbf{r}'$ around \mathbf{r}' is to be found in a volume $d\mathbf{r}$ around \mathbf{r} after the lapse of a time interval t . Value $\rho(\mathbf{r}')$ is the equilibrium density of the diffusing molecular species. $M(\mathbf{k}, t)$ is the amplitude of the spin echo measured in the idealized PFG experiment, where t is the time separating the gradient pulses, and \mathbf{k} is a wave vector defined by the gradient pulses, $\mathbf{k} = \gamma \int_0^\delta \mathbf{g}(t) dt$. In this formula, γ is the gyromagnetic ratio, δ the width of the gradient pulse, and \mathbf{g} is the gradient vector during the pulse. The normalization constant $M(\mathbf{0}, t) \equiv M(t)$ at zero wave vector is time-dependent, and reflects the attenuation of the NMR signal in the absence of applied gradient pulses. The normalised amplitude $M(\mathbf{k}, t)/M(t)$ is usually the quantity of interest in the present context.

The propagator $G(\mathbf{r}, \mathbf{r}', t)$ satisfies the equations

$$\frac{\partial G(\mathbf{r}, \mathbf{r}', t)}{\partial t} = D_0 \nabla^2 G(\mathbf{r}, \mathbf{r}', t) , \quad (2)$$

$$G(\mathbf{r}, \mathbf{r}', t = 0^+) = \delta^3(\mathbf{r} - \mathbf{r}') , \quad (3)$$

$$D_0 \hat{\mathbf{n}} \cdot \nabla G(\mathbf{r}, \mathbf{r}', t) + \rho G(\mathbf{r}, \mathbf{r}', t) \Big|_{\mathbf{r} \in \Sigma} = 0 , \quad (4)$$

where $\hat{\mathbf{n}}$ is an outward (from pore to grain) directed normal vector at the pore–grain interface, Σ , and the parameter ρ [11] is the strength of spin relaxation at the interface. D_0 is the free diffusion constant.

The time-dependent diffusion coefficient $D(t)$ is defined in three dimensions as $\langle r^2(t) \rangle / (6t)$ where $\langle r^2(t) \rangle$ is the mean square displacement of spins in time t . Note that the angle brackets include an average over all possible initial positions for the diffusing species. In the presence of surface relaxation, the mean square displacement is calculated only for spins that survive at time t . Note that the diffusion coefficient is in general a tensor; we assume it to be isotropic for simplicity, and the generalisation to the anisotropic case is straightforward. In terms of the normalised amplitude, $D(t)$ is given by

$$D(t) = -\frac{1}{t} \lim_{k \rightarrow 0} \frac{\partial}{\partial k^2} \frac{M(k, t)}{M(t)}. \quad (5)$$

In the bulk fluid, where no restrictions are present, we have $D(t) = D_0$. Analogously, the RTO probability $P(t)$ is given by

$$P(t) = \frac{1}{2\pi^2} \int_0^\infty M(k, t) k^2 dk. \quad (6)$$

In practice, the integral over wave vectors have a cut-off determined by the maximum possible gradient strengths in the experimental apparatus. In the bulk fluid, one has the free RTO probability $P_0(t) = (4\pi D_0 t)^{-3/2}$. It is useful to define a dimensionless enhancement of RTO probability caused by the restrictions, $R(t) = P(t)/P_0(t)$.

3. Short-time expansion

At short times, the restrictions to free diffusion are only felt by a layer of walkers within a diffusion length near the interface. In this limit, the time-dependence of the quantities $P(t), D(t)$ are governed only by the averaged local properties of the interface. The quantity $P(t)$ has been studied extensively before, usually in the context of a somewhat distinct physical picture that can be obtained by expressing $P(t)$ in terms of the eigenvalues of the Laplace operator in the pore space with boundary conditions appropriate to the problem at hand. Defining E_n through the eigenvalue equation $D_0 \nabla^2 \psi_n(\mathbf{r}) = -E_n \psi_n(\mathbf{r})$ where $\psi_n(\mathbf{r})$ satisfies appropriate boundary conditions at the pore wall, we have the identity $P(t) = \sum_{n=0}^\infty e^{-E_n t}$. The quantity $P(t)$ as given by the above equation is referred to in other contexts as the ‘spectral sum’, or the ‘partition function’, and makes its appearance in the well-known problem of ‘hearing the shape of a drum’ [12]. In this context, it is well known that $P(t)$ has a short-time expansion in powers of \sqrt{t} , where the coefficients of successive terms depend only on averaged local properties of the pore surface. For the partially absorbing boundary conditions which are of relevance to this paper, and for piecewise smooth pore interfaces, it can

be shown that the normalised RTO probability satisfies [7]

$$R(t) = 1 + \frac{\sqrt{\pi}}{2} \frac{S}{V_p} (D_0 t)^{1/2} - \left[\frac{1}{3} \left\langle \frac{1}{R_1} + \frac{1}{R_2} \right\rangle + \frac{\rho}{D_0} \right] \frac{S}{V_p} (D_0 t) + \mathcal{O}((D_0 t)^{3/2}). \quad (7)$$

Here D_0 is the diffusion constant of the bulk fluid, S/V_p is the surface-to-volume ratio of the pore space, ρ is the surface relaxivity, and R_1 and R_2 are the principal radii of curvature of the interface. The signs of R_1, R_2 are chosen so that they are positive for the outside of a sphere. For simplicity, we have omitted terms arising from the presence of kinks in the pore surface, which correct the coefficient of the linear term in the above expansion. An analogous expansion has been derived for the time-dependent diffusion coefficient $D(t)$ [4,13]:

$$\begin{aligned} \frac{D(t)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}} \frac{S}{V_p} (D_0 t)^{1/2} - \frac{S}{6V_p} \left(\frac{1}{2} \left\langle \frac{1}{R_1} + \frac{1}{R_2} \right\rangle - \frac{\rho S}{V_p} \right) (D_0 t) \\ + \mathcal{O}((D_0 t)^{3/2}). \end{aligned} \quad (8)$$

The linear in-time corrections to this equation arising from kinks in the pore surface can be found in [13]. In biological porous media, where the interfaces are weakly permeable, the leading order term in the expansions continues to hold, while the permeability appears in the subleading term, analogous to the surface relaxivity [14].

The above expressions have the important implication that the leading order term in $D(t), P(t)$ depends only on the surface-to-volume ratio. In turn, this implies that these time-dependent quantities could be used to measure the surface-to-volume ratio, which is an important geometrical parameter characterising the porous medium. The leading order behaviour for $D(t), P(t)$ has been verified in experiments in artificial porous media consisting of polystyrene or glass spheres packed randomly and saturated with fluid, as well as in some clean sandstones [6,16].

An interesting observation, based on numerical simulations, is that $R(t)$ is described by the leading order term in the short-time expansion for significantly longer times than $D(t)$. The author is not aware of a simple explanation of the accuracy of the leading term in $R(t)$ at times at which the next order corrections would nominally be large.

4. Intermediate and long times

While at short times $P(t), D(t)$ carry information about local properties of the pore surface, at long times they provide information about the connectivity of the pore space. However, expansions analogous to Ref. [13] cannot be found in general. At long times, as long as the pore space is sufficiently well connected, the diffusion coefficient has a limit, usually denoted by the effective diffusion constant, which is related to the effective conductivity of the medium when saturated with a conducting fluid [17]. In the absence of other length scales in the problem, one may expect a smooth crossover from the short-time behaviour presented above, to the long-time asymptote. While the

crossover is difficult to compute for a realistic geometry, a Padé approximant can be found that has the right limiting behaviour but captures the crossover accurately [6]. An interesting feature of the crossover is that it can be quite rapid, and the diffusion coefficient falls close to its long-time value even before the diffusing species have time to diffuse to the neighbouring pores. This explains the lack of time-dependence of $D(t)$ in typical measurements in biological tissue, where the shortest measurement times are still too long to capture the short-time transient from the bulk to the effective diffusion coefficient. This has led in the past to the erroneous conclusion that diffusion in such tissue is not restricted by cell membranes [8].

One case of particular interest is the diffusion of water protons in brain tissue, where a rapid reduction of the effective diffusion coefficient is observed following stroke. The effective diffusion tensor in normal brain tissue is in general anisotropic, and 2–10 times smaller than bulk water. This is due to the impeding effect of cell membranes. Stroke is accompanied by the swelling of cells and concurrent reduction in extracellular space, which has been implicated in the reduction of the effective diffusion coefficient. Using theoretical as well as experimental models, it has been argued [14] that the effective diffusion coefficient is dominated by the tortuosity of the extracellular space, which is increased on cellular swelling. An effective medium formula for the effective diffusion coefficient relevant to such tissue may be found in Ref. [14].

In sedimentary rocks, the long-time behaviour of the diffusion coefficient in PGSE experiments is fairly variable [15]. In some clean sandstones, the behaviour parallels that of the model sphere-pack geometries. In most carbonates, however, the long-time asymptote is not approached. There are multiple possible reasons for this, the most probable one being that the carbonates are heterogeneous beyond the maximum diffusion lengths reached ($<100\ \mu$).

At long times, the momentum dependence of the PGSE amplitude deviates from Gaussian behaviour due to the modulation of the diffusive wave packet by the structure of the porous medium [3,4]. This leads to ‘diffraction-like behaviour’ in the PGSE amplitude, dramatically illustrated in experiments on fluid-saturated sphere packs by the appearance of a peak at a wave vector corresponding to the inverse of the sphere size [3]. A phenomenological ansatz has been used to understand the behaviour of the PFG amplitude at long times [4]. The ansatz implies that the PFG amplitude is given approximately by the convolution of a Gaussian with the Fourier transform of the density–density correlation function of the pore space. The ansatz can be shown to be exact for periodic geometries at long times and predicts the development of ‘Bragg peaks’ in $M(k, t)$ at the reciprocal lattice vectors. Another manifestation of the diffraction-like behaviour is that $M(k, t)$ is predicted at large wave vectors to decay as $1/k^4$.

From the ansatz, it follows that the asymptotic form of the normalised RTO probability is given by (for $\rho = 0$) [7]

$$\lim_{t \rightarrow \infty} R(t) = \frac{1}{\phi} \left(\frac{D_0}{D_{\text{eff}}} \right)^{3/2}. \quad (9)$$

The prediction is exact for periodic three-dimensional geometries, but we expect it to continue to hold even for non-periodic geometries, as long as the pore space remains connected in three-dimensions, and a long-time effective diffusion constant can be defined. Recently, the prediction has been verified experimentally in experiments on fluid-saturated sphere packs [18]. An interesting feature of the intermediate-time behaviour of $R(t)$ is the appearance of a maximum at a diffusion time corresponding to diffusion across a pore, which has been observed in numerical simulations in both periodic and random sphere-pack geometries, and is consistent with the experimental observations. An argument for the presence of such a maximum may be made on theoretical grounds for a periodic pore space [18].

Unlike model porous media like packed spheres, sandstones and carbonate rocks do not show clear diffraction-like behaviour [7]. Instead, the deviations from Gaussian behaviour are smooth and featureless. Interestingly, the curves giving the non-Gaussian momentum dependence of $M(k, t)$ at different diffusion times can be collapsed onto each other using an appropriate formula where the momentum is scaled by the diffusion length [7,19]. One interpretation of this phenomenon is that over the NMR time scale, the diffusion is locally Gaussian but anisotropic, an average over the axis of anisotropy producing the deviation from Gaussian behaviour at large wave vectors. In rock samples studied in Ref. [7], based on the behaviour of $R(t)$ it appears that over the NMR time scale (~ 100 ms) the diffusion is locally one-dimensional.

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