Diffusion Propagator as a Probe of the Structure of Porous Media

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We propose a simple ansatz that relates the diffusion propagator for the molecules of a fluid confined in a porous medium to the pore-space structure factor. Theoretical arguments and numerical simulations show that it works well for both periodic and disordered geometries. The ansatz allows us to deconvolve structural data from momentum dependent pulsed field gradient spin-echo data.

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In a classic paper entitled "Can one hear the shape of a drum?," Kac [1] considered the problem of determining the geometry of the boundary from the eigenvalues of the diffusion equation in a region surrounded by perfectly absorbing walls. More recently, de Gennes [2] discussed an analogous problem related to the decay of magnetization in a region where the relaxation rate at the boundary is infinite.

The present paper is concerned with extracting information related to the morphology of porous media from the wave vector ($\mathbf{k}$) and time (t) dependent pulsed field gradient spin-echo (PFGSE) amplitude, $M(\mathbf{k},t)$ [3-7]. Physically, $M(\mathbf{k},t)$ is the spin-echo amplitude in which the dephasing and rephasing of the transverse magnetization are modulated by two sharp gradient pulses [i.e., the z component of the magnetic field is changed by $\mathbf{g}\cdot\mathbf{r}f(t)$, where $f(t)=0$ except for two intervals, a distance t apart, each of duration δ]. If a spin originally at position $\mathbf{r}$ diffuses to $\mathbf{r}_1$ at time t, its net phase change is $\gamma\delta\mathbf{g}\cdot(\mathbf{r}-\mathbf{r}_1)$, where γ is the gyromagnetic ratio. The wave vector $\mathbf{k}=\gamma\delta\mathbf{g}$ is therefore a tunable parameter. Formally, $M(\mathbf{k},t)$ is given by the diffusion propagator [3-7] for a fluid molecule confined to the pore volume, V_p,

$$M(\mathbf{k},t)=\frac{1}{V_p}\int d\mathbf{r}\,d\mathbf{r}_1\,e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_1)}G(\mathbf{r},\mathbf{r}_1,t)\,, \tag{1}$$

which satisfies the equation

$$\begin{gathered}\frac{\partial G(\mathbf{r},\mathbf{r}_1,t)}{\partial t}=D_0\nabla^2G(\mathbf{r},\mathbf{r}_1,t),\quad t>0\,,\\ G(\mathbf{r},\mathbf{r}_1,t=0^+)=\delta(\mathbf{r}-\mathbf{r}_1)\,.\end{gathered} \tag{2}$$

Here D_0 is the bulk molecular diffusion constant and the reflecting boundary condition, $\hat{\mathbf{n}}\cdot\nabla G(\mathbf{r},\mathbf{r}_1,t)|_{\mathbf{r}\in\Sigma}=0$, is imposed at the pore-grain interface Σ.

We are concerned with how the spectrum *and* eigenfunctions associated with Eq. (2) are influenced by the structure of the pore-grain interface. This problem is of interest because recent papers [5,6] indicate that PFGSE measurements may provide a probe of the pore geometry over a range of length scales (0.10 → 10 μm) not accessible to standard techniques like x-ray and small-angle neutron scattering. We emphasize, however, that the relationship (1) between the PFGSE amplitude and the morphology of the pore space is not clear-cut. To simplify this relationship we propose a simple ansatz that links the measured amplitude directly to the pore-space correlation function. In periodic systems, a combination of analytic results and computer simulations indicates that the ansatz provides an excellent approximation to $M(\mathbf{k},t)$. In addition, simulations on disordered sphere packs are in good accord with the recent experimental results of Callaghan *et al.* [6].

To extract geometrical information from the propagator G, consider, first, the short-time regime, $(D_0t)^{1/2}\ll a$, where a is a typical pore size. We assume that the pore surface is locally flat, and not a fractal. In the short-time regime, only walkers within a distance $(D_0t)^{1/2}$ from the walls, of area S, sense the presence of the walls. Thus, only a fraction $S(D_0t)^{1/2}/V_p$ of the total number of walkers deviate in their behavior from a free random walk, and the deviation of the propagator from a free Gaussian is also of this order. To be more specific, the fact that near a flat reflecting wall the Green's function is the sum of a free Gaussian and its image implies [7] that the effective diffusion coefficient at time t, $D(t)=\langle|\mathbf{r}(t)-\mathbf{r}(0)|^2\rangle/2dt$, varies as

$$\frac{D(t)}{D_0}=1-\frac{4}{3d\sqrt{\pi}}\frac{(D_0t)^{1/2}S}{V_p}+O(D_0t)\,, \tag{3}$$

as $t\to0^+$ where d is the spatial dimension. Provided the pore surface is isotropic, the coefficient of k^2 in the logarithm of the PFGSE amplitude at time t is simply $tD(t)$. It should therefore be possible to extract the surface to volume ratio experimentally from the PFGSE amplitude using this procedure. We will see that the accuracy of Eq. (3) is supported by numerical simulations.

Next consider the long-time regime $(D_0t)^{1/2}\gg a$. While an exact representation of the propagator for an arbitrary pore geometry is difficult to obtain, the essential physics is straightforward. The diffusion propagator in free space is a Gaussian. The propagator in a porous medium can be thought of as a Gaussian modulated by the presence of excluded regions, i.e., as a Gaussian with the grain space cut out of it. For an isotropic pore space, this idea can be encapsulated in the following phenomenological ansatz, $G_A(\mathbf{r}-\mathbf{r}_1,t)$, for the propagator averaged over the mean position of the initial and final points [i.e., over $(\mathbf{r}+\mathbf{r}_1)/2$]:

$$G_A(\mathbf{r}-\mathbf{r}_1,t)=\frac{C(t)}{[4\pi D_1(t)t]^{d/2}}\exp\left[-\frac{(\mathbf{r}-\mathbf{r}_1)^2}{4D_1(t)t}\right]S(\mathbf{r}-\mathbf{r}_1),\quad t\geq 0. \tag{4}$$

Here $S(\mathbf{r}-\mathbf{r}_1)$, the connected pore-space structure function, is defined in terms of the characteristic function $\chi(\mathbf{r})$ [$\chi(\mathbf{r})=1$ for $\mathbf{r}$ in the pore space and $\chi(\mathbf{r})=0$ for $\mathbf{r}$ in the solid phase],

$$S(\mathbf{r}-\mathbf{r}_1)=\frac{1}{V_p}\int d\mathbf{R}\,\chi(\mathbf{r}+\mathbf{R})\chi(\mathbf{r}_1+\mathbf{R}). \tag{5}$$

In Eq. (4), $C(t)$ is a normalization constant and $D_1(t)$ is an effective width of the Gaussian. These parameters are determined by the simultaneous conditions

$$\int d\mathbf{r}\,G_A(\mathbf{r},t)=1, \tag{6a}$$

$$\int d\mathbf{r}\,G_A(\mathbf{r},t)r^2=\langle|\mathbf{r}(t)-\mathbf{r}(0)|^2\rangle=2dt\,D(t). \tag{6b}$$

[The integrations in (5) and (6) extend over the entire volume of the system.] By construction, the ansatz satisfies a diffusion equation (with a frequency and wave vector dependent diffusion constant) that reduces to the true coarse-grained diffusion equation at long wavelengths and times. In the Laplace–wave-vector domain, $sG_A(k,s)=-k^2D_A(k,s)G_A(k,s)+1$, where from Eqs. (6) it follows that $\lim_{s\to 0^+}[\lim_{k\to 0}D_A(k,s)]=D_{\mathrm{eff}}$ where $D_{\mathrm{eff}}\equiv\lim_{t\to\infty}D(t)$ is the macroscopic diffusion constant. In momentum space, the ansatz predicts that

$$M_A(\mathbf{k},t)=C(t)\int\frac{d\mathbf{k}_1}{(2\pi)^d}\exp[-(\mathbf{k}-\mathbf{k}_1)^2D_1(t)t][\phi(2\pi)^d\delta(\mathbf{k}_1)+\tilde{S}(\mathbf{k}_1)]\geq 0, \tag{7}$$

where $\tilde{S}(\mathbf{k})\equiv\int d\mathbf{r}\,e^{\mathbf{k}\cdot\mathbf{r}}[S(\mathbf{r})-\phi]\geq 0$ is the Fourier transform of $S(\mathbf{r})-\phi$, and ϕ is the porosity (i.e., the volume fraction occupied by the pore space). We emphasize that the inequality $\tilde{S}(\mathbf{k})\geq 0$ guarantees that the ansatz will always yield a positive definite PFGSE amplitude. Note that $R\to\infty$, $S(R)\to\phi$. For an isotropic geometry, $\partial S(R)/\partial R\to -S/4V_p$, one quarter of the surface to volume ratio [8], as $R\to 0$ (excluding fractally rough surfaces). The large k behavior of $M_A(\mathbf{k},t)$ is therefore related to S/V_p. Thus, the ansatz implies that the PFGSE amplitude, $M_A(\mathbf{k},t)$, is an effective Gaussian plus the Fourier transform of the structure function of the pore space convoluted with the same effective Gaussian. For the cases considered below it turns out that $D_1(t)\approx D(t)$; thus one obtains a formula with a single phenomenological input, i.e., the effective diffusion constant, $D(t)$, which can be extracted from the k^2 dependence of measured $M(k,t)$.

In the case of periodic geometries, it can be shown that the ansatz reproduces certain exact results. There the propagator may be evaluated in terms of eigenfunctions [7] which satisfy the Bloch-Floquet theorem: $\psi_{n\mathbf{q}}(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}u_{n\mathbf{q}}(\mathbf{r})$, where n is a band index, the function $u_{n\mathbf{q}}(\mathbf{r})$ has the translational periodicity of the underlying Bravais lattice, and $\mathbf{q}$ is a vector in the first Brillouin zone of the reciprocal lattice. Given an arbitrary momentum vector $\mathbf{k}$, the magnetization density can be written as $M(\mathbf{k},t)=\sum_n e^{-E_n(\mathbf{q})t}|\tilde{u}_{n,\mathbf{q}}(\mathbf{K})|^2$. Here $\mathbf{K}$ is the unique reciprocal-lattice vector that returns $\mathbf{k}$ to the first zone, i.e., $\mathbf{k}=\mathbf{q}+\mathbf{K}$ and $\tilde{u}_{n,\mathbf{q}}(\mathbf{K})\equiv\Omega_p^{-1}\int\exp(i\mathbf{K}\cdot\mathbf{r})u_{n,\mathbf{q}}(\mathbf{r})d\mathbf{r}$ with the integration confined to a single unit cell whose pore volume is Ω_p. The splitting between the two lowest bands is of the order of D_0/a^2, where a is the lattice constant. For $t\gg a^2/D_0$, the lowest band controls the above sum and, assuming that the effective mass tensor is isotropic [i.e., that $E_0(\mathbf{q})\approx q^2D_{\mathrm{eff}}$], we have

$$M(\mathbf{k},t)=e^{-(\mathbf{k}-\mathbf{K})^2D_{\mathrm{eff}}t}|\tilde{u}_{0,\mathbf{q}}(\mathbf{K})|^2\quad(q\ll a^{-1}). \tag{8}$$

Remarkably, $M(\mathbf{k},t)$ *does not decay* as $t\to\infty$ when $\mathbf{k}=\mathbf{K}$. In other words "Bragg peaks" appear in $M(\mathbf{k},t)$ at reciprocal-lattice vectors. The ansatz for periodic geometries is

$$M_A(\mathbf{k},t)=C(t)\sum_{\mathbf{K}}e^{-(\mathbf{k}-\mathbf{K})^2D_1(t)t}|\tilde{\chi}(\mathbf{K})|^2. \tag{9}$$

Since $u_{0,\mathbf{0}}(\mathbf{r})=\chi(\mathbf{r})$, the characteristic function of the pore space, is the solution of the diffusion equation with eigenvalue zero, Eq. (9) becomes exact $t\to\infty$. The right-hand side of (9) is a sum of Gaussians, all of the same width, centered around reciprocal-lattice vectors, with heights given in terms of the Fourier transforms: $\tilde{\chi}(\mathbf{K})=\Omega_p^{-1}\int\exp(i\mathbf{K}\cdot\mathbf{r})\chi(\mathbf{r})d\mathbf{r}$. Thus, for a connected periodic pore space of *arbitrary* shape, a knowledge of $M(\mathbf{k},\infty)$, which is a set of delta functions, specifies the lattice geometry completely.

At intermediate times, the propagator can only be calculated numerically. We have performed random walk simulations [9,10] on several ordered grain consolidation (GC) models [11]. The results of simulations show that the ansatz is a good approximation even at intermediate times. The approximation $D_1(t)=D(t)$ has been used to calculate $M_A(\mathbf{k},t)$, $D(t)$ being an input from the simulation. Typical results are shown in Fig. 1, where data for a simple cubic model is displayed for a given direction of the k vector. We can see that the two sets of curves corresponding to $M_A(\mathbf{k},t)$ and $M(\mathbf{k},t)$ almost overlay each other even at intermediate times, although there are deviations near the minima where the values obtained from the simulations are dominated by statistical noise. We

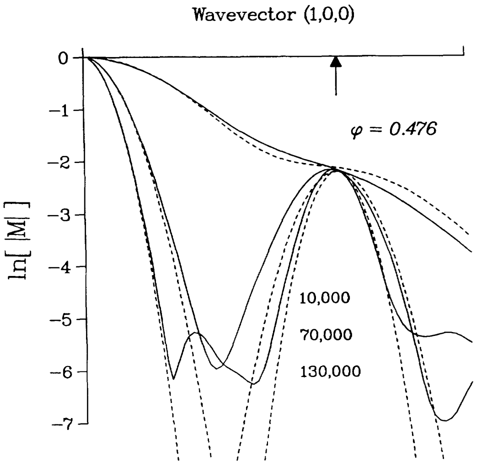

FIG. 1. Comparison of the ansatz (dashed curves) with numerical simulations (solid curves) based on a simple cubic sphere pack. The wave vector is taken in the (100) direction. The three comparisons correspond to 10000, 70000, and 130000 random walk time steps. Similar agreement is seen for other directions in **k** space and for other periodic structures.

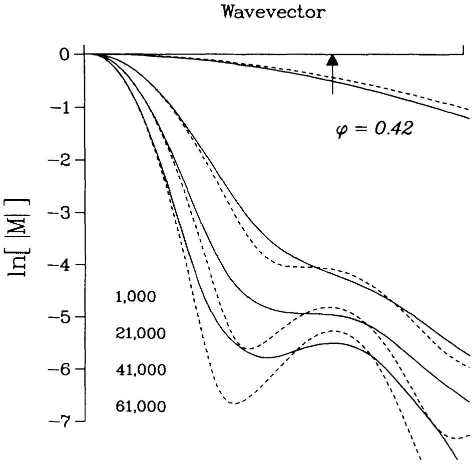

FIG. 3. Comparison of the ansatz (dashed curves) with numerical simulations (solid curves) based on an unconsolidated random sphere pack. The arrow on the horizontal axis marks the wave vector $k = 2\pi/(2R_0)$. The four comparisons correspond to 1000, 21000, 41000, and 61000 random walk time steps.

conclude, therefore, that the ansatz is at least qualitatively correct at all times for these and related periodic geometries.

Consider, next, disordered model systems based on random sphere packings. We have considered two systems, the first being an unconsolidated packing ($\phi = 0.42$) and the second a system in which the porosity is reduced to $\phi = 0.26$ by the standard GC algorithm of uniform grain growth [11]. The normalized structure functions, $S_0(R) \equiv (1-\phi)^{-1}[S(R)-\phi]$ for these two systems are shown in Fig. 2. To check the accuracy of Eq. (3), we have looked in detail at the short-time behavior of the diffusion constant $D(t)$ for the $\phi = 0.42$ system. The inset in Fig. 2 shows that the agreement is excellent. A comparison of the results of diffusion simulations [9,10] and the ansatz (computed with the structure factors shown in Fig. 2) is given in Figs. 3 and 4. In both cases, the two are found to be in reasonable agreement. Callaghan *et al.* [6] have measured PFGSE amplitudes for water saturated random packings of polystyrene spheres with radius $R_0 = 8$ μm. Their data show a rounded peak in the PFGSE amplitude (similar to the structure seen in Fig. 3) at around $k = 2\pi/(2R_0)$. These authors interpret their data in

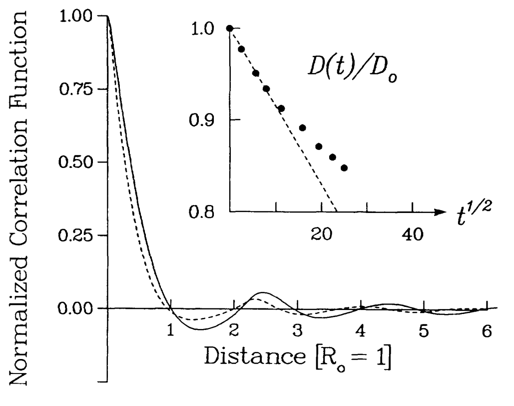

FIG. 2. The normalized pore-space correlation function, $S_0(\mathbf{R})$, is shown for a $\phi = 0.426$ random sphere pack (solid curve) and for the same packing consolidated to $\phi = 0.260$ (dashed curve). The $\phi = 0.426$ case corresponds to the experimental situation discussed in Ref. [6]. Inset: The initial behavior of the diffusion constant $D(t)$ (solid dots) compared with the prediction of Eq. (3) (dashed line) for $\phi = 0.426$ packing. The value of S/V_p was calculated from the $R \rightarrow 0$ limiting behavior of $S(R)$.

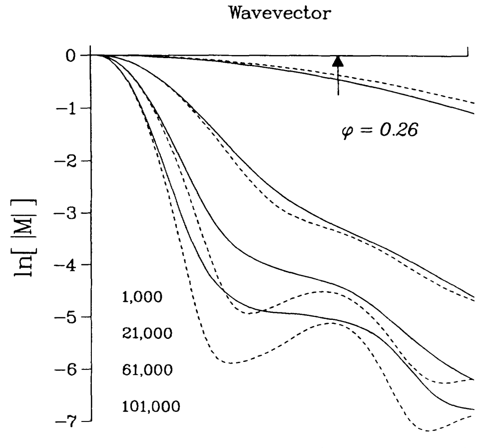

FIG. 4. Comparison of the ansatz (dashed curves) with numerical simulations (solid curves) based on a consolidated random sphere pack. The arrow on the horizontal axis marks the wave vector $k = 2\pi/(2R_0)$. The six comparisons correspond to 1000, 21000, 61000, and 101000 random walk time steps.

terms of a simple model, consisting of identical pores connected weakly by narrow necks, so that the magnetization is uniform within each pore. This model, which can be likened to a tight-binding model, is inapplicable to their and many other experimental systems, which consist of a well-connected pore geometry. The models and techniques developed here are consistent with the data presented in Ref. [6], but are considerably more general.

There are two difficulties in analyzing real systems. First, there are internal inhomogeneities in the magnetic field, which should cause the observed signal to be different from Eq. (1). Experimentally, this problem may be reduced by multipulse variants of the stimulated echo sequence. Second, is the problem of enhanced surface relaxation [7] which may be taken into account by calculating the propagator for partially absorbing boundary conditions, characterized by a surface relaxation strength ρ. We find that, for small ρ, the PFGSE signal in presence of surface relaxation, $M(k,t|\rho)$, is approximately the product of the total magnetization $M(0,t|\rho)$ and the PFGSE amplitude $M(k,t|\rho=0)$. Thus we have $M(k,t|\rho)\approx M(0,t|\rho)M(k,t|\rho=0)$; the amplitude of the packet decays in time, while its shape is not greatly altered. One may then analyze the PFGSE amplitude as a function of k at different fixed times by normalizing the amplitudes to the same value at $k=0$ (which removes the dominant effect of ρ), and treating the resulting normalized amplitudes according to the analysis given in the paper for $\rho=0$.

In conclusion, the PFGSE amplitude probes two kinds of information about the geometry of the pore space: (a) at short times, it probes the surface to pore volume ratio S/V_p; and (b) at long times, it probes (i) the *connected* structure factor of the pore space, and (ii) through the diffusion constant it probes the connectivity and tortuosity of the pore space. We have presented an exact result for the short-time behavior, and an ansatz which models the propagator, for all time and wavelength scales, that should provide a model-independent way of interpreting PFGSE data, especially at long times. The analysis should also be useful in interpreting other experiments that measure the diffusion propagator in porous media, e.g., light scattering experiments from polymers in the pore space of Vycor glass [12], where a strong deviation is seen in the momentum space propagator from a Gaussian form at large values of momentum.

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