

● *Invited Lecture***THE CHARACTERISATION OF FLUID TRANSPORT IN POROUS SOLIDS BY MEANS OF PULSED MAGNETIC FIELD GRADIENT NMR**

K.J. PACKER, S. STAPF, J.J. TESSIER, AND R.A. DAMION

Department of Chemistry, University of Nottingham, Nottingham, UK

The determination, by pulsed field gradient (PFG) nuclear magnetic resonance (NMR), of the probability distributions (propagators) of displacements for fluids undergoing transport by both flow and self-diffusion within porous solids is outlined. The nature of the observed propagator, $P_{\Delta}(Z)$, for the transport of a single aqueous phase through an outcrop sandstone (Fontainebleau) is described. Recent measurements of the propagators for both aqueous and oil phase flow in the limiting saturation states of irreducible water (S_{wi}) and residual oil (S_{or}) in the same sample are illustrated through the use of difference propagators. These are shown to emphasise the regions of the propagators most affected by the presence of the second, stationary, phases in these limiting saturation conditions. Measurement of the propagators for both oil and aqueous phases undergoing simultaneous flow are also described for the same sandstone sample and the effect of increasing S_{wi} on the nature of the oil flow is briefly discussed. Finally, a new two-dimensional (2-D) experiment is introduced which measures the propagator $P_{\Delta}(X, Z)$. This is the joint probability for displacements X and Z in time Δ . Some preliminary observations of these two-dimensional propagators are shown for single-phase flow in the Fontainebleau sandstone sample, where Z and X are, respectively, displacements in the axial and radial direction for the cylindrical sample for which the pressure gradient is along Z and where bulk radial flow is constrained to be zero. © 1998 Elsevier Science Inc.

Keywords: Flow; Pulsed field gradient NMR; Displacement distributions; Sandstones; Two-phase flow; Self-diffusion.

INTRODUCTION

The transport of liquids within porous solid matrices is important in a wide variety of circumstances such as oil and gas production, heterogeneous catalysis, water resource management, performance of consumer products such as detergent powders, etc. Apart from macroscopic phenomenological observation of the relationships between fluid outputs and inputs there are only very few experimental methods which can investigate these processes within the, often optically opaque, solid matrices. Of these, nuclear magnetic resonance (NMR) is one of the most versatile.^{1,2} NMR imaging methods are of value in cases where the scale of the fluid-filled porosity is consistent with the resolution/signal-to-noise limitations of the technique and the sample has heterogeneities at scales greater than the resolution. For systems with pore

scales below the practical resolution of imaging the pulsed magnetic field gradient (PFG) technique is extremely valuable.³ A considerable literature exists concerning the use and interpretation of such PFG NMR measurements for single-phase diffusion of fluids within porous solids. More recently, several groups have used PFG NMR to investigate the transport by both flow and diffusion in porous solids.^{4–8}

In these measurements, the PFG NMR method is used to determine the so-called propagator, $P_{\Delta}(Z)$, which is the probability distribution of fluid displacements, Z , occurring in a time Δ . The direction of Z is determined by the direction of the field gradient used and can be altered with respect to the sample under study. In this paper, we review the general behaviour of such propagators for the flow and diffusion of fluids in porous materials such as oil reservoir rocks where the pore size scales are typi-

Address correspondence to Dr. K. J. Packer, Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK. E-mail: Ken.Packer@nottingham.ac.uk

Current address for J.J. Tessier: Zeneca Pharmaceuticals, Dept. CAM, Alderley Park, Macclesfield, Cheshire SK10 4TF, UK

cally in the 1–100 μm range and report preliminary results for an experiment which determines the joint probability distribution, $P_\Delta(X, Z)$, for displacements in the two directions X and Z .

MATERIALS AND METHODS

The PFG NMR Experiment and Fluid Flow in Porous Solids

The basic equation underlying the use of the PFG NMR experiment has the form:

$$S_\Delta(q_z) = S_0 \int P_\Delta(Z) \exp\{-iq_z Z\} dZ \quad (1)$$

where $S_\Delta(q_z)$ is the NMR signal measured in a PFG experiment comprising the equivalent of two magnetic field gradient pulses separated by a time Δ and where $q_z = (1/2\pi)\gamma\delta g_z$, with δ and g_z being the duration and amplitude of these pulses. Experimentally, $S_\Delta(q_z)$ is determined by variation of q_z and Fourier transformation then yields the propagator $P_\Delta(Z)$. Eqn (1) requires that any displacements during δ are negligible in the context of those occurring during Δ .

In applications to fluid transport in porous solids the usual method used is the so-called alternating pulsed gradient stimulated-echo (APGSTE) pulse sequence which is designed to minimise effects of internal field gradients arising from magnetic susceptibility differences between the fluids and the solid matrix and to allow as large a range of Δ as possible by making use of the (usually) longer T_1 timescale compared with T_2 .⁹

All results reported here were obtained using a GE Ω CSI NMR system, operating for ^1H NMR at 85 MHz and equipped with an S-150 Acustar actively shielded gradient coil set, an Oxford Instruments 31-cm bore magnet and a GE birdcage radiofrequency coil. Typically, the APGSTE pulse sequence was used with 32 values of q_z , between $\pm q_{\text{max}}$ with zero-filling to double the data set before complex Fourier transformation. Measurements on the sandstone sample used in this study were made using a specially designed flow cell, described elsewhere.⁴

Propagators for Single-Phase Flow

The usual geometry of flow experiments is a cylindrical sample of the porous solid with the flow driven by an axial pressure difference between the two faces of the cylinder with bulk radial flow constrained to be zero. In all the following discussion, $Z = \{z(\Delta) - z(0)\}$, is taken as axial with X , correspondingly, in the radial direction with respect to the cylindrical sample.

A number of groups have reported studies of the propagators for single-phase flow in various porous solid matrices, either fabricated from glass beads or naturally

occurring materials.^{4–7} The general behaviour found for $P_\Delta(Z)$ can be understood as the transition between two limiting behaviours at short and long Δ . To the extent that displacements arising from flow are larger than those from self-diffusion, for short Δ the propagator is essentially a projection of the instantaneous velocity field of the flowing fluid onto the Z axis, i.e., molecules maintain constant velocity during Δ . For long times Δ , fluid molecules have sampled most of the velocity field, leading to dispersion, and self-diffusion has also allowed molecules to sample the different velocities present. Under these circumstances the propagator tends to a Gaussian shape, with a maximum moving along the Z axis with the average velocity. At intermediate times the detailed shapes of the propagators depend on the properties of the particular pore space. Figure 1 illustrates the type of propagator behaviour which has been found.⁴ Several groups have undertaken modelling of these propagators using a variety of approaches. These methods have reproduced many of the main features observed but, as yet, the direct interpretation of the NMR-determined propagator in terms of the underlying properties of the pore space has not been achieved. Figure 2 shows a typical best simulation fit to experimental data for one such approach.⁷

At this point, it is worth noting that imaging studies of fluid flow tend to rely on the measurement of a single average phase shift for the spins in each voxel. This is because the signal-to-noise ratio available at any reasonable spatial resolution makes determination of the complete propagator for each voxel of insufficient precision in a reasonable time. However, this average phase shift is related to the first moment of the appropriate propagator. Thus, any interpretation of such “velocity” images must consider the effect of changes in flow rates, observation times or other experimental parameters on the underlying propagators which may change shape considerably over the range of parameters employed.

Propagators for Two-Phase Saturations

Single-phase flow. We have undertaken extensive measurements of propagators for a sample of Fontainebleau sandstone (porosity 25%; permeability 2 Darcy) containing two immiscible fluids (3% NaCl brine and dodecane).⁸ There are two limiting cases where only one phase is flowing, namely irreducible water saturation, S_{wi} , and residual oil, S_{or} . Figure 3 shows the difference propagators P^o where:

$$P^o = [P_\Delta(Z, S_{wi} = 0.2) - P_\Delta(Z, S_{wi} = 0.03)] \quad (2)$$

for the flowing oil phase at a constant volume flow rate of oil of 200 mL/h and a range of values of Δ . The two

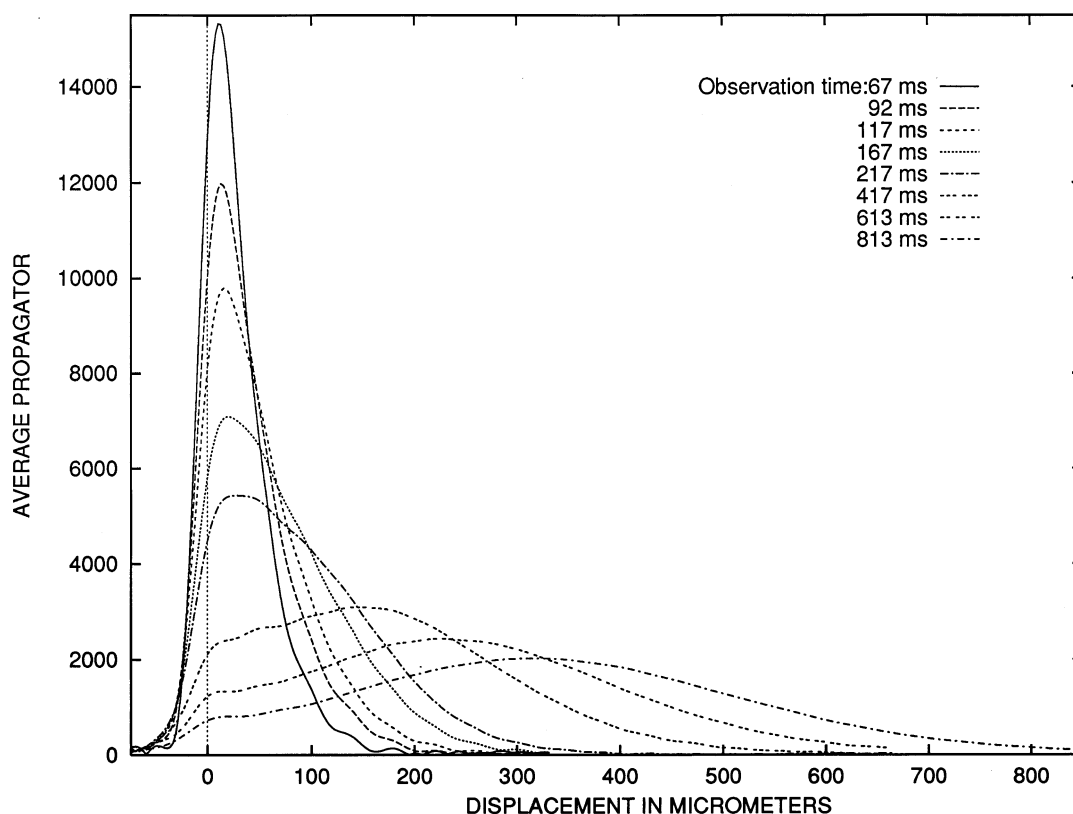


Fig. 1. The average propagator, $P_{\Delta}(Z)$ for water transport in Fontainebleau sandstone (see text for details) at the different observation times Δ as indicated. (Reproduced with permission of Taylor and Francis from Ref. 4.)

different values of S_{wi} were achieved by flowing dodecane into the sample, initially at $S_w = 1$, at 200 mL/h, and then, 1000 mL/h. It was assumed that returning the volume flow rate of oil to 200 mL/h, following the flow at 1000 mL/h, did not change the distribution of the water phase.

Figure 4 shows similar plots of the difference propagator P^{ω} , where:

$$P^{\omega} = [P_{\Delta}(Z, S_{or} = 0.2) - P_{\Delta}(Z, S_w = 1)] \quad (3)$$

for a constant water flow rate of 400 mL/h and for a range of values of Δ . The $S_{or} = 0.2$ saturation state was achieved by flowing the aqueous phase into the sample, initially at $S_{wi} = 0.03$, at 400 mL/h.

As all propagators are normalised, the total areas under the difference propagators P^o and P^{ω} are zero. The characters of the $P^{\omega/o}$ reflect a number of features of the single phase flow in the different saturation states.

Firstly, the non-flowing phase occupies a fraction of the pore space leading to a larger average displacement (velocity) for a fixed volume flow rate. In fact, the first moment of P^{ω} , for example, is given by:

$$\int Z P^{\omega} dZ = \Delta v^* [(S_w^b - S_w^a)/S_w^b S_w^a] \quad (4)$$

where v^* is the interstitial velocity, given by $Q/\phi A$, with Q the volume flow rate, ϕ the porosity and A the cross-sectional area of the sample. The two saturation states used in P^{ω} are labelled by a and b . In Fig. 4, for example, the predicted first moment of P^{ω} for $\Delta = 812$ ms, is $79.6 \mu\text{m}$, based on the measured S_{or} of 0.2 (from chemical shift resolved spectrum). The value found from P^{ω} is $73 \mu\text{m}$.

A further effect of the presence of a second, non-flowing, phase is that there is an increase in the fraction of molecules which maintain displacements close to zero for given Δ . This can be seen in both Figs. 3 and 4 in the strong positive values near zero displacement. This must arise because of an increase in stagnant regions of the flow field either because of the creation of dead-ends or an increase in the diffusion path lengths required for molecules starting in low values of the velocity field to reach the faster flow lines. A corollary of this is that, as already mentioned, there must be an increase in the velocity of a fraction of the molecules in order to maintain constant Q . Thus, not only the average velocity

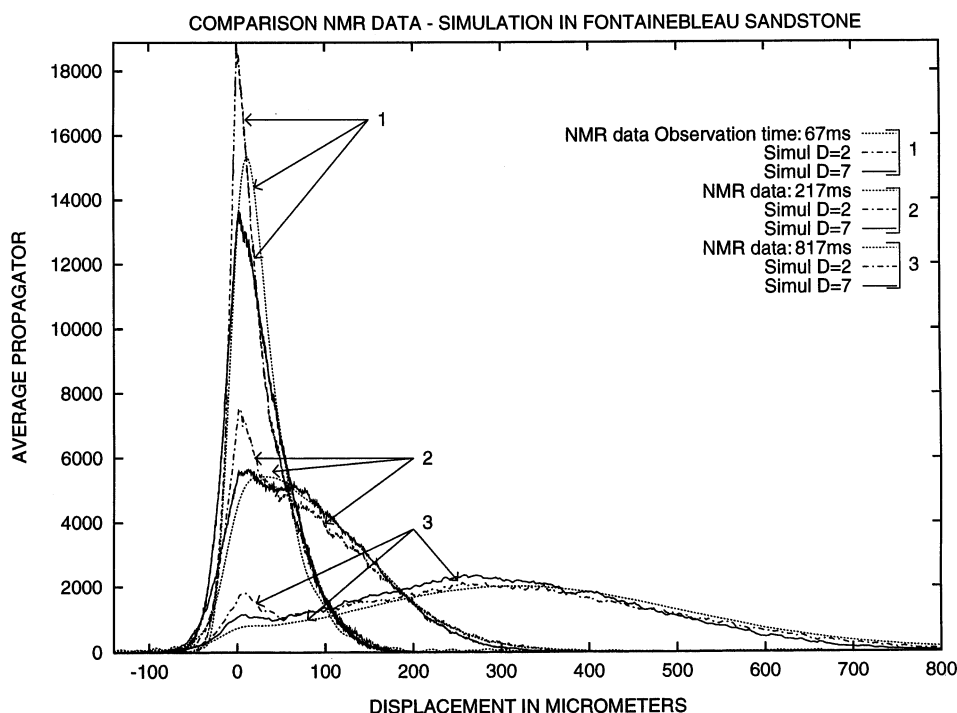


Fig. 2. A comparison of observed and simulated average propagators, $P_{\Delta}(Z)$ for water transport in Fontainebleau sandstone (see text for details). The best fits are obtained by adjusting the value of D to $7.10^{-9} \text{ m}^2\text{s}^{-1}$ (see Ref. 7 for details). (Reproduced by permission of the American Institute of Chemical Engineers. Copyright ©1997 AIChE. All rights reserved.)

increases but there is an increased dispersion of displacement distribution to both small and larger values leading to the alternating positive/negative/positive character of $P^{o/\omega}$ as a function of Z at fixed Δ .

Modelling of these behaviours is currently being undertaken.

Two-phase flow. Using the same sample, we have measured the propagator of both oil and aqueous phases for situations in which flow of both phases is maintained at chosen volume flow rates. The simultaneous propagator measurement is made possible in this case by the fact that the oil and water ^1H NMR signals are resolvable through their chemical shifts. Figure 5 illustrates the flow propagators, at fixed Δ , for both oil and water phases for two different relative flow rates. In interpreting the changes observed, it should be recalled that the saturations will change in response to the fractional flows and that the sample is a water-wet sandstone. What is clear is that, as the water flow rate and, hence, saturation is increased, the oil flow is carried by a decreasing fraction of the reduced oil saturation. Further details can be found elsewhere.⁸

Two-Dimensional (2-D) Propagators

Recently, we have extended the PFG NMR approach to an experiment which determines the 2-D

propagator $P_{\Delta}(X, Z)$, which is the joint probability for a displacement X and Z . Full details of this experiment and a complete set of results will be published elsewhere (Packer and Stapf, unpublished data). Here, we note that, as with any 2-D NMR experiment, two variables, in this case q_x and q_z , are varied over their appropriate ranges followed by Fourier transformation of the signal $S_{\Delta}(q_x, q_z)$ to give the required 2-D propagator.

For a sample comprising a bulk fluid for which the only transport mechanism is isotropic self-diffusion, the 2-D propagator exhibits circular symmetry and has a gaussian cross-section at any angle in the X, Z plane.

Figure 6, on the other hand, shows the corresponding 2-D propagator for water undergoing flow in the Fontainebleau sandstone mentioned earlier. What is clear from this figure is that there are correlations between X and Z displacements within this material under these conditions. This is evidenced by the shapes of the contours of constant probability. In order to illustrate this further, Fig. 7 shows a plot of the function $\{P_{\Delta}(X, Z) - P_{\Delta}(X)P_{\Delta}(Z)\}$. In the limit that X and Z are independent, $P_{\Delta}(X, Z) = P_{\Delta}(X)P_{\Delta}(Z)$ and the difference function would be zero at all points in the X, Z plane. As can be seen from Fig. 7 this is clearly not

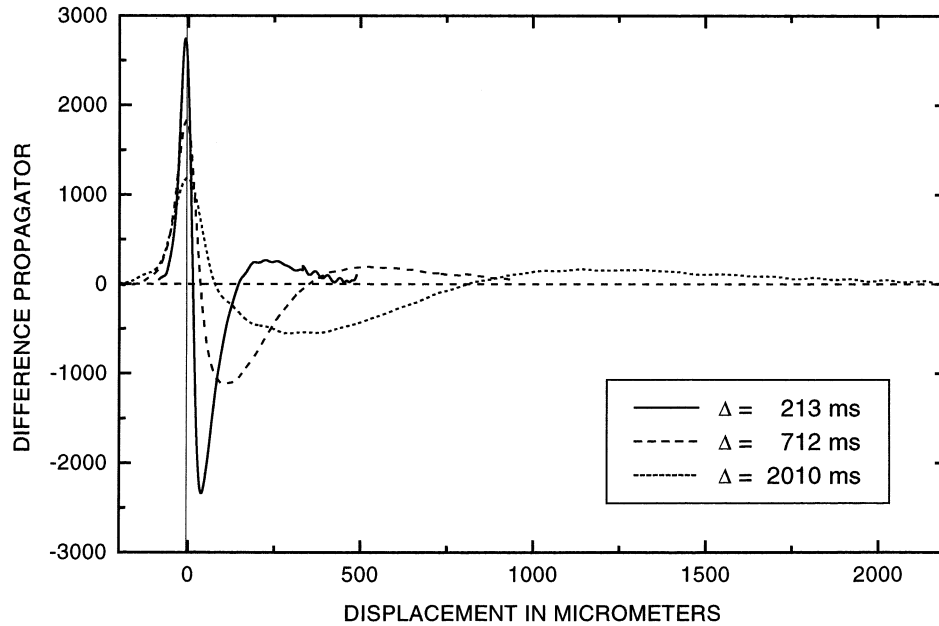


Fig. 3. The difference propagator P^o , as defined in the text, for oil flow in Fontainebleau sandstone at two different S_{wi} states. The reference state, $S_{wi} = 0.03$, can be thought of as approximating to single phase saturation with oil. As described in the text these plots show clearly the effect of the presence of the wetting phase ($S_{wi} = 0.2$) in causing a fraction of spins to move more slowly (peak near zero displacement) with another fraction, moving faster, given that the volume flow rate is constant.

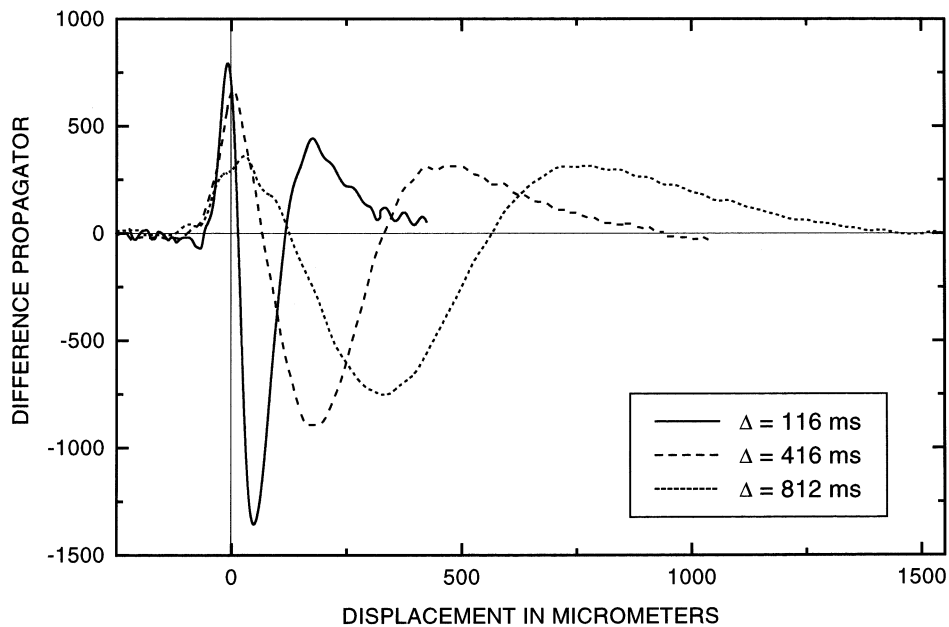


Fig. 4. The difference propagator P^w , as defined in the text, for water flow in Fontainebleau sandstone at S_{or} and $S_{wi} = 1$. The effect of the presence of the residual oil appears similar to that in Fig. 3. However, quantitative evaluation of the relative areas of the positive peaks in both P^o and P^w , for a larger set of Δ values than displayed in these figures, reveals clear differences in the variation with Δ .

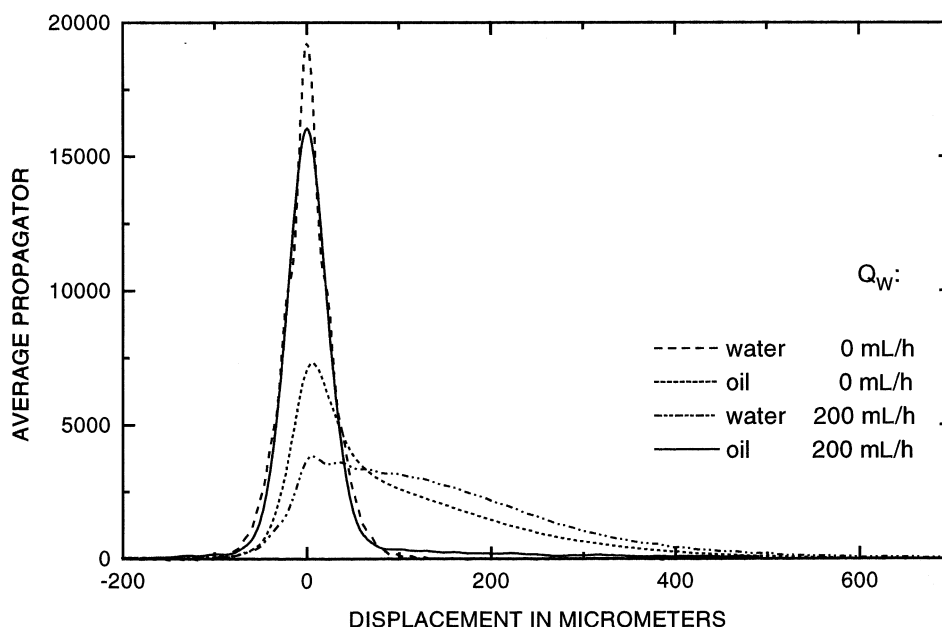


Fig. 5. The oil and water propagators for two-phase flow through Fontainebleau sandstone. $\Delta = 415$ ms for all measurements and $Q^o = 200$ mL/h. Q^w takes the two values shown in the key. The important feature is that, as Q^w is increased, the oil and water propagators behave differently, the former increasing its intensity near zero displacement, the latter evolving in a similar manner to that found for single-phase flow.

the case. The forms of these difference propagators, such as shown in Fig. 7, should be characteristic of the nature of the flow-field imposed on the fluid by the pore space topology and scale.

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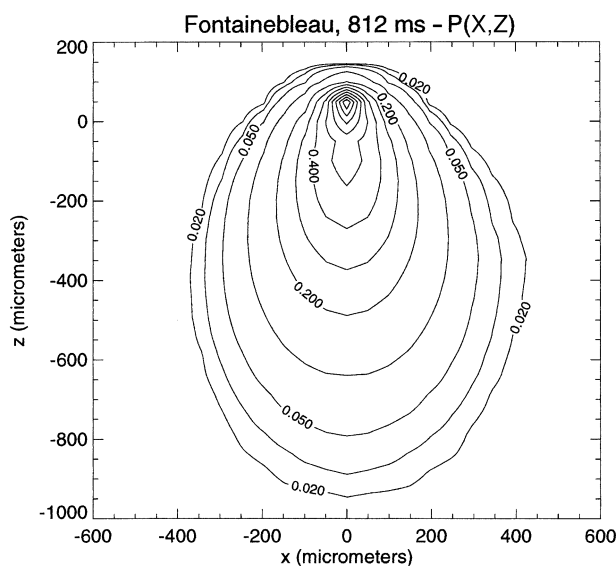


Fig. 6. The 2-D propagator $P(X, Z)$ for water flow in a Fontainebleau sandstone for $\Delta = 812$ ms and $Q = 400$ mL/h. The maximum intensity of the plot is set to unity.

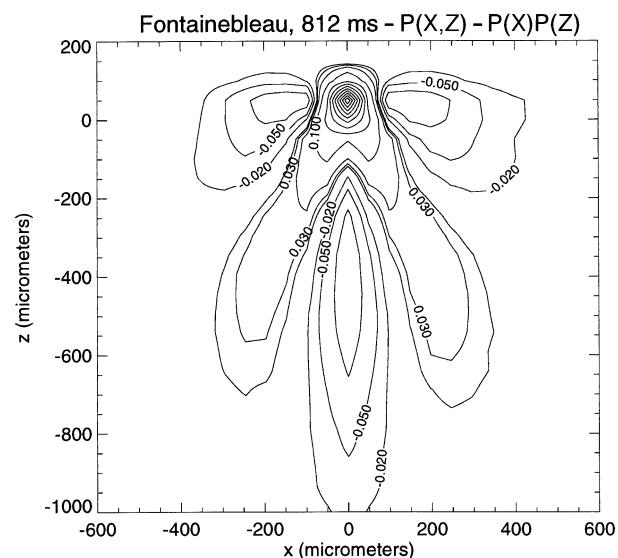


Fig. 7. The 2-D difference propagator $\{P(X, Z) - P(X)P(Z)\}$ for water flow in a Fontainebleau sandstone for $\Delta = 812$ ms and $Q = 400$ mL/h. The maximum intensity of the plot is set to unity.

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