A novel approach to interpretation of the time-dependent self-diffusion coefficient as a probe of porous media geometry

V.V. Loskutov [a,b,*], V.A. Sevriugin [a]

[a] Physics and Mathematics Department, Mary State University, Lenin Sq. 1, Yoshkar-Ola 424000, Russia
[b] Baker Hughes, Russian Science Center, Kutateladze 4A, Novosibirsk 630128, Russia

ABSTRACT

This article presents a new approximation describing fluid diffusion in porous media. Time dependence of the self-diffusion coefficient $D(t)$ in the permeable porous medium is studied based on the assumption that diffusant molecules move randomly. An analytical expression for time dependence of the self-diffusion coefficient was obtained in the following form: $D(t) = (D_0 - D_\infty)\exp(-\sqrt{D_0 t/\lambda}) + D_\infty$, where D_0 is the self-diffusion coefficient of bulk fluid, D_∞ is the asymptotic value of the self-diffusion coefficient in the limit of long time values ($t \to \infty$), λ is the characteristic parameter of this porous medium with dimensionality of length. Applicability of the solution obtained to the analysis of experimental data is shown. The possibility of passing to short-time and long-time regimes is discussed.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

During recent years, understanding of confined fluid dynamics in different environments and modifications of its structure has often been in the focus of scientific research. The topic is of great relevance in many technological areas as well as in living systems, where essential fluid related phenomena occur in restricted geometries of porous structures, biological cells, their membranes and surfaces, active sites of proteins, etc. [1,2]. The scientific interest is centered on the development of efficient measuring methods, among which the spin echo with the non-uniform magnetic field has gained a decisive role.

NMR techniques are well known as non-invasive methods for study of a wide variety of porous materials. By detecting the ^{1}H signal from water-saturated rocks and model systems, information including the surface-area-to-volume ratio S/V [3,4], average pore size [5–7], and visualizations of fluid transport under flow [8] can be obtained. Usually, these methods study diffusion of the water spins, and the Pulsed Gradient Spin Echo (PGSE) technique has become a powerful tool for this purpose [9, 10]. Except in the cases of very small pores, however, spin relaxation quenches the NMR signal before water molecules can diffuse across even one pore. For this reason, liquid phase NMR has been unable to yield measurements of the long-range properties of most porous media; e.g., tortuosity in reservoir rock samples [3,11] – an important parameter that describes pore connectivity and fluid transport though the rock.

It should be noted that, as a result of researching various porous systems, fairly general experimental [12–14] and theoretical [15–19] approaches to describing self-diffusion in the porous and heterogeneous systems have been developed. One of the key approaches to studying the porous media by means of NMR-diffusometry is analyzing time dependence of the self-diffusion coefficient, which enables one to determine and establish relationships between such parameters of the porous medium as the ratio of pore surface area to pore volume, tortuosity, permeability, connectedness, electric conductivity, and the bulk self-diffusion coefficient of pore fluid [11].

The NMR method with the pulsed gradient of the magnetic field enables one to measure mean-square displacements or, which is the same thing, the self-diffusion coefficient of fluids or gases as function of diffusion time [9]. In closed isolated volumes or pores of the porous system, where diffusive displacement of molecules is limited by the pore size, the effective self-diffusion coefficient drops to zero at $t \to \infty$ [20]. In the porous medium with connected pores, the effective self-diffusion coefficient at $t \to \infty$ has a certain finite asymptotic limit D_∞ [3,21,22].

Typically, except for trivial cases, it is quite difficult to solve a diffusion equation. For this reason, dependence between geometry of the porous medium and the self-diffusion coefficient of the molecules has been solved analytically for a limited number of simple geometry types only. It should be noted that, as of today, there is no theory describing the self-diffusion coefficient over the entire range of observation times available during diffusion experiments.

It is a common practice to divide time dependence of the self-diffusion coefficient into two regimes: (i) Short-time diffusion regime, when mean-square displacements of molecules are much smaller than the linear pore size. In this case, only the molecules

---

* Corresponding author at: Physics and Mathematics Department, Mary State University, Lenin Sq. 1, Yoshkar-Ola 424000, Russia. Fax: +7 8362 56 57 81.
E-mail address: val_losk@rambler.ru (V.V. Loskutov).

next to the limiting surface at the initial moment of measurement time will have a non-zero probability of hitting the pore wall. For the molecules which did interact with the pore surface, the diffusive propagation factor is not Gaussian, unlike that for the molecules in bulk fluid. (ii) Long-time regime when mean-square displacements of molecules are much greater than the linear pore size. The diffusant molecules equally "feel" the influence of the limiting surfaces, and molecular motion is averaged over the entire pore space.

The solution to the problem of time dependence of the self-diffusion coefficient $D(t)$ of fluid contained in the porous medium with smooth boundaries for short times was found in [17]. The general expression of time dependence $D(t)$ is as follows:

$$\frac{D(t)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}} \frac{S}{V} \sqrt{D_0 t}, \tag{1}$$

where S and V are the surface area and pore volume, respectively.

Furthermore, according to [3], the short-time formulae Eq. (1) has important implications. First: it may be more natural to use $\sqrt{t}$ as the coordinate for dependence $D(t)$ rather than $\log(t)$, as in earlier publications [9,23]. Second: the first term in Eq. (1) contains a concrete factor, and thus, taking into account $\sqrt{t}$, the initial slope of dependence $D(t)$ leads to a method of finding S/V.

If the effects of enhanced relaxation of pore boundaries can be neglected, then for large t, $D(t)$ approaches an asymptotic limit of D_∞ according to [24]

$$D(t) = D_\infty + \frac{(D_\infty - D_0)\theta}{t} + \vartheta\left(\frac{1}{t^{3/2}}\right), \tag{2}$$

where θ is a fitting parameter that has a unit of time and appears to scale with bead size [3,4].

As it can be seen from this quick review, there is no general approach for describing the complete time dependence of the self-diffusion coefficient in porous structure. In this paper, we report results of NMR experiments in randomly packed spherical glass beads. We describe a method of determining geometrical parameters of porous media using the time-dependent diffusion coefficient of fluid molecules in fluid-saturated porous media as measured by the Pulsed Field Gradient (PFG) technique [9,10].

In Fig. 1 we show time dependence of the normed self-diffusion coefficient $D(t)/D_0$ as a function of diffusion length $\sqrt{D_0 t}$ for dibromomethane and acetontrile in the pores of sphere pack: average a sphere diameter 49 μm; Solid Line 1 is a short-time approach (Eq. (1)), Solid Line 2 is a function proportional to t^{-1} (see Eq. (2)).

2. Materials and methods

2.1. Materials

It is well known that the NMR echo signal observed in a PFG experiment has a Fourier relationship to the probability of spin motion – the so-called displacement propagator [25,26], which can be viewed as the spectrum of motion. The spin-echo signal obtained in a PFG experiment can be written as follows:

$$\Psi(q, t) = \int F(\mathbf{R}, t) \exp(i\mathbf{q}\mathbf{R}) d\mathbf{R}, \tag{3}$$

where $F(\mathbf{R}, t)$ is the ensemble average displacement propagator or the probability of the spin with displacement $\mathbf{R}$ proceeding during diffusion time t. $\mathbf{q}$ is the wavevector of the magnetization modulation induced in the spin by the field gradient pulse of strength g and pulse duration δ: $\mathbf{q} = \gamma\delta\mathbf{g}$, where γ is the spin magnetogyric ratio. In limit of small q, the echo will be attenuated by the following factor [8]: $\exp(-q^2 D(t)t)$, where $D(t) = R^2/6t$ is the time-dependent diffusion coefficient describing incoherent random motion of the spin
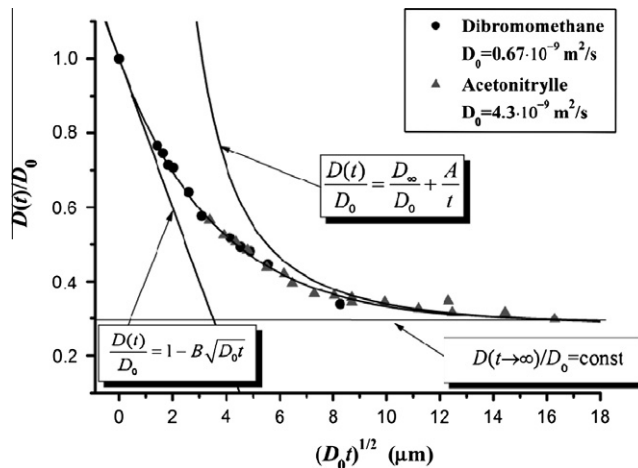
Fig. 1. Time dependence of the diffusion coefficient measured for dibromomethane and acetonitrile fluids in randomly packed spherical glass beads with average diameter 49 μm plotted vs. the diffusion length $\sqrt{D_0 t}$. The limits at short-t (see Eq. (1)) and long-t (Eq. (2)) are shown by lines 1 and 2, respectively, while the solid curve represents exponential function of Eq. (4) type. Horizontal line 3 shows the asymptotic value at $t \to \infty$.

in porous space. $D(t)$ will vary as a function of t, with more spins encountering obstacles to their motion as t increases.

Samples of randomly packed spherical glass beads of different sample diameters were prepared. Cylindrical glass cells held the bead packs. Each cell contained beads with bead diameters ranging from 44 μm to 300 μm. The basic characteristics of these porous media are listed in Table 1.

In Table 1, the ratio S/V was then calculated via the following formula for random bead packs $\frac{S}{V} = \frac{6(1-\phi)}{d\phi}$ [27], where ϕ is the sample's porosity and d is the average bead diameter. Porosity of ϕ = 0.37 was used, appropriate for a random packing of spheres. The effective pore diameter d_{SV} was defined as the diameter of the pore with the same ratio S/V as the sphere: $d_{SV} = 0.2836d$.

Before the experiments, all glass bead samples were kept in acid to rid them of surface paramagnetics. Samples of beads saturated with fluids were prepared by drying the beads in an oven at 150 °C for several hours and then pouring enough fluid under dry atmospheric conditions to just overfill the pores. The excess of fluid was then allowed to evaporate until the samples reverted to dry appearance. The saturated samples were placed in 5 mm NMR tubes and sealed after filling the free space in the tube with a Teflon plug in order to minimize evaporation of the adsorbed liquid.

At short diffusion times, the effective diffusion coefficient approached the molecular diffusion coefficient D_0. This value was determined in a separate experiment on a bulk fluid sample under identical conditions. The characteristics of the fluids used are listed in Table 2.

2.2. Self-diffusion coefficient measurements

The pulsed field gradient NMR measurements were carried out on the PFG NMR spectrometer constructed at the Molecular

Table 1
Major characteristics of the porous media under study.

Bead size, μm	Average bead size, μm	S/V ratio, μm^{-1}	Effective pore diameter d_{SV}, μm
44–53	49	0.208	14
53–63	59	0.173	17
63–74	69	0.148	20
74–88	81	0.126	23
100–200	150	0.068	42.5
200–300	250	0.041	71