УЧЕНЫЕ ЗАПИСКИ КАЗАНСКОГО ГОСУДАРСТВЕННОГО УНИВЕРСИТЕТА
Том 147, кн. 2 Физико-математические науки *2005*

UDK 539.217+539.143.3+532.72

PULSED FIELD GRADIENT NMR STUDY OF THE TRANSLATIONAL MOBILITY IN POROUS MEDIA: RESTRICTED DIFFUSION, INTERNAL MAGNETIC FIELDS, FLOWS AND MOLECULAR EXCHANGE

V.D. Skirda, A.R. Mutina, R.V. Archipov

Abstract

The basic principles of the pulse field gradient NMR (PFG NMR) study of porous media are discussed in the article. It is shown that self-diffusion coefficient of the fluid molecules confined in the porous media dependence on the diffusion time includes direct information about restriction sizes within porous matrix. The question of the inducted in the porous media internal magnetic fields is discussed from the point of view of the required using of the high pulse field gradients in order to avoid experimental data distortion.

It is shown that information about porous media structure and fluid localization could be obtained by the study of the diffusion decay in the internal field gradients (without applying pulse field gradient). The experiment where one can study dependence of the stimulated echo amplitude on the time interval between first and second RF pulses (τ-scanning) with different diffusion times is offered to get information about internal magnetic field gradient (IMFG) distribution. The offered approach of data analysis allows to evaluate IMFG values and width of their distribution. Particularly, is shown the in the partially saturated porous media the information about internal magnetic field gradients allows to conclude about fluid localization in the porous matrix.

One of the topical questions of the fluid filtration through the porous media problem is the question of the "stagnant" zone quantitative characterization. The possibilities of the PFG NMR technique are demonstrated in the paper: registration of the fluid molecules share in the "stagnant" zones, determination of the characteristics of the molecular exchange between "stagnant" zone molecules and molecules involved in the flow, etc.

PFG NMR possibilities to study exchange process between different fluid phases in the porous media are discussed. Particularly, it shown that the apparent population of the molecules in the different "phases" dependence on the diffusion time allows one to obtain information not only about average molecular life-time in the phase, but also information about distribution function of the life times.

Introduction

The spatial and time resolution of the PFG NMR technique is directly proportional to the amplitude of the magnetic field gradient. In the standard NMR equipment (for example, NMR scanners) the typical gradient amplitude is limited to 1 T/m. Using such gradient pulses it is possible to investigate translational displacements of fluid molecules on the distances only about a few microns. Producing higher magnetic field gradients involves serious technical difficulties. Nevertheless, while in the 1980s the maximum amplitude of PFG did not exceed 10 T/m, at present magnetic field gradients of about 100 T/m and higher are used in several laboratories. For a long time we used pulse gradient with maximum amplitude up to 50–100 T/m. With a special probehead, we have achieved real gradient values up to 500 T/m. This considerably broadens the scope of the method and its applications. It also opens up a new window to study porous media by PFG NMR in the range beyond the sub-micron level. Some preliminary measurements demonstrate the potential of this NMR technique to characterize the pore space over distances below 1 μm. Such information is essential for the study of the relationships between the pore geometry and transport properties of porous media.

1. General principles

PFG NMR study of the translational dynamics of molecules is based on the recording of the loss of spin phase coherence as a result of their translational motion in the magnetic field gradients. Information about diffusion processes can be obtained by analysing the diffusion decay $A(\bar{q}, t)$ – the dependence of the spin-echo signal amplitude on magnetic field gradient parameters and time t. The $\bar{q}$ vector is an analogue of the wave vector and is equal to $\bar{q} = (2\pi)^{-1}\gamma\delta\bar{g}$, where γ is the gyromagnetic ratio of resonating nuclei, $\bar{g}$ is the amplitude and δ is the duration of the magnetic field gradient. The diffusion decay $A(\bar{q}, t)$ can be described by van Hove correlation function

$$A(q,t) = \iint \rho(r) P_s(r; r', t) \exp(i2\pi q(r' - r))\, dr dr',$$

where $\rho(r)$ is the initial density of spins and $P_s(r; r', t)$ is is the probability of observing a spin at a point with radius vector r' at time t, if at the initial time the spin was located in the point with radius vector r. PFG NMR method has a wide range of applications due to direct relation between $P_s(r; r', t)$ and $A(q, t)$. In the case of free diffusion in a one-component system the probability $P_s(r; r', t)$ is given at the time-scale longer than microscopic times by the Gaussian function

$$P_s(\bar{r}, \bar{r}', t) = \frac{1}{(4\pi D_s t)^{3/2}} \exp\left\{ -\frac{|\bar{r}' - \bar{r}|^2}{4 D_s t} \right\},$$

where D_s is the self-diffusion coefficient, the root-mean-square displacement for free diffusion is $\left\langle [\bar{r}'(t) - \bar{r}(0)]^2 \right\rangle = 6 D_s t$ (Einstein equation).

For a single-phase system (with a single D_s value) and provided $\delta g \gg \tau g_0$, where g_0 is the constant magnetic field gradient, the diffusion decay for the most widely used stimulated spin-echo sequence (Fig. 1) is expressed as

$$A(2\tau, \tau_1, g^2) = A(2\tau, \tau_1, 0) \exp\left(-q^2 D_s t\right).$$

In the case of exponential relaxation we have

$$A(2\tau, \tau_1, 0) = \frac{A(0)}{2} \exp\left(-\frac{2\tau}{T_2} - \frac{\tau_1}{T_1} \right),$$

where $A(0)$ is the initial amplitude of the free induction decay after the first 90° pulse; T_2 is the spin-spin relaxation time; T_1 is the spin-lattice relaxation time; τ and τ_1 are the time intervals between the first and second and between the second and third 90° radiofrequency pulses, respectively; Δ is the time between gradient pulses; and $t \equiv t_d = (\Delta - \delta/3)$ is the diffusion time. For a simple one-component system, there is no difference in the way to obtain diffusion decay: variable parameter could be Δ, $\bar{g}$ or δ.

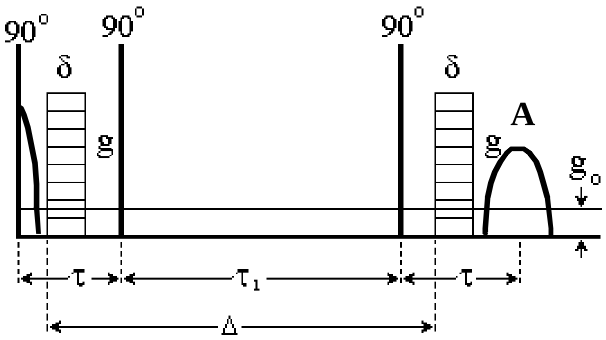

Fig. 1. Stimulated echo pulse sequence

2. Investigation of porous media structure by pulsed field gradient NMR

Self-diffusion of liquids confined in porous media was found to be non-Gaussian. The shape of the diffusion echo decay (DD) is not exponential and the average self-diffusion coefficient D depends on the diffusion time. It was shown recently that analysis of the diffusion data for a liquid confined in a porous structure can be used to obtain structural information about the porous medium [1–6]. The shape of diffusion decay dependence on the diffusion time contains information about the media molecules diffuse in; however, it has not been studied until now. Analytical equations for DDs were obtained only for systems with rather simple structures, when pores are randomly distributed in channels [7–9], layers [8, 10, 11] and spherical or cylindrical cavities [6, 8, 12].

It was found [4, 6] that another way to obtain information about porous media is studying the dependence of D on diffusion time. The behaviour of the mean self-diffusion coefficient of a liquid in a porous structure is indicative of the existence of three diffusion time ranges:

(i) Short time range, when the root-mean-square displacements of molecules of a liquid are smaller than the linear pore dimensions, and there is no substantial effect of pore walls on the observed self-diffusion coefficient; that is $D^* \approx D_0$, where D_0 is the self-diffusion coefficient of bulk liquid.

(ii) Intermediate diffusion time range, when the root-mean-square displacements of molecules of a liquid are comparable to the linear pore dimensions and the effective coefficient D^* depends on the diffusion time.

(iii) Long diffusion time range. The behaviour of D^* is then determined by the structure of the porous space (porosity, permeability, etc.).

For closed pores fully restricted diffusion with $D^* = D^{\mathrm{eff}}(t) \propto t^{-1}$ can be observed at long diffusion time. Experimental data can then be used to determine linear restriction sizes by the Einstein equation $R_p^2 \approx 6D^{\mathrm{eff}}(t) \cdot t$.

For connected pores and long diffusion times, the root-mean-square displacements of molecules are larger than the pore dimensions, and the motion of the liquid becomes averaged over the space of the system. For porous systems with a random structure, diffusion decay in this case is usually exponential and is characterized by a diffusion-time-independent effective self-diffusion coefficient $D^* = D_\infty$.

Thus, the behavior of the mean self-diffusion coefficient of molecules in a restricted geometry system is determined by three terms, namely, the self-diffusion coefficient of the pure liquid, the effect of restrictions, and the permeability effect. According to [1,

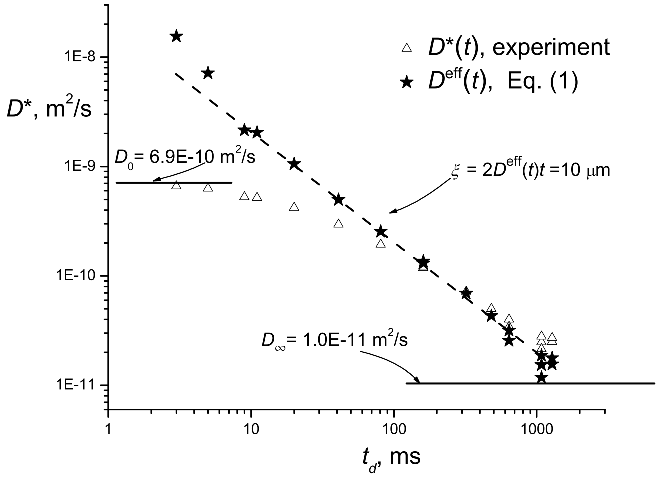

Fig. 2. Experimentally obtained $D^*(t)$ – dependence for the porous media filled on the 20% with tridecane (triangles) and calculated with Eq. (1) $D^{\text{eff}}(t)$ dependence (stars). Dashed line indicates $D \propto t^{-1}$

2], these effects can be separated correctly by scaling equation

$$D^{\text{eff}}(t) = [D^*(t) - D_\infty] \cdot \left[\frac{D_0}{D_0 - D^*(t)}\right]. \tag{1}$$

The $D^{\text{eff}}(t)$ dependence can be used to obtain information about restriction dimensions (porous medium characteristics) by analysing the overall time dependence of the self-diffusion coefficient, including the three principal time ranges. One of the main characteristics of the $D^{\text{eff}}(t)$ function is that $D^{\text{eff}}(t) \propto t^{-1}$ and restrictions sizes can be calculated even in the case of the partially permeable system.

As an example of using these technique, in Fig. 2 we show the data for the tridecane average self-diffusion coefficient dependence on the diffusion time $D^*(t)$ for the quartz sand with average particle size 90 μm partially (20%) saturated with tridecane at room temperature. The objective of the study was to obtain information about fluid localization in the partially saturated porous media. One of the assumptions was that fluid molecules could be localized as a "drops". If this assumption is correct, one can expect to obtain the dependence of self-diffusion coefficient of the molecules in these drops on diffusion time as a restricted one. In Fig. 2 experimentally obtained $D^*(t)$ dependence is shown with triangles: within the diffusion time range from 3 ms to 1 s average self-diffusion coefficient of the tridecane molecules changes even more than in one order of magnitude. Nevertheless, obtained $D^*(t)$ dependence does not correspond to fully restricted diffusion (the slope $D \propto t^{-1}$ is shown with a dashed line in the figure). Thus, fluid molecules are localized in the porous space as some connected areas ("drops"). To calculate their characteristic sizes we used Eq. (1) – calculated $D^{\text{eff}}(t)$ dependence is shown in Fig. 2 with stars. As one can see from the figure, $D^{\text{eff}}(t)$ dependence has a slope "-1" and was used to evaluate the characteristic restriction ("drops") size that was found to be $\xi = \sqrt{\bar{r}^2} = \sqrt{6tD^{\text{eff}}(t)} \approx 10$ μm.

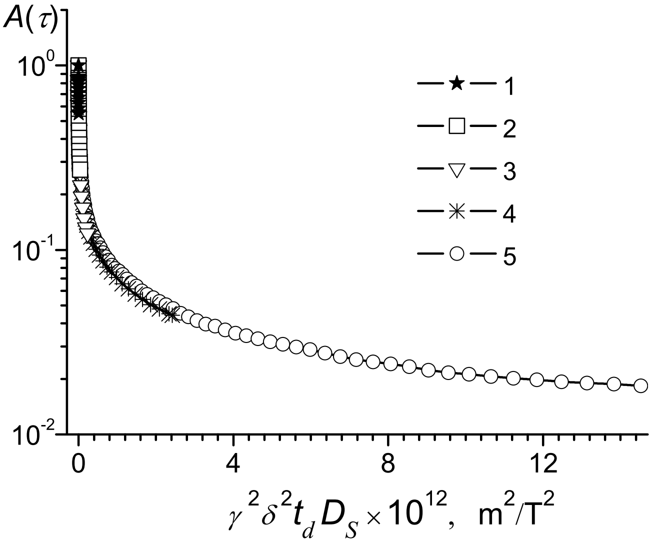

Fig. 3. Diffusion decays $A(\tau)$ obtained for tridecane in sand at Δ: 5 ms (stars); 8 ms (squares); 10 ms (triangles); 20 (snowflakes) and 320 ms (circles)

3. Diffusion of liquid molecules in the internal magnetic field gradients (IMFG)

When the molecular mobility is studied by NMR diffusometry and NMR relaxometry in in species with a different magnetic susceptibility $\Delta\chi$ between different parts of the system (for instance, between porous matrix and liquid), the presence of internal magnetic field gradients (IMFG), $\bigtriangledown\vec{H} \propto \Delta\chi$, has to be taken into account to interpret the experimental results correctly. For porous materials filled with a liquid, IMFG values and their distribution over the sample depend on the external magnetic field, $\vec{H}_0$, on the morphology of the porous medium and on the magnitude of $\Delta\chi$. Thus, the IMFG corresponds to the geometry and properties of the porous medium. However, for the most real porous materials it is extremely difficult both to define the characteristics analytically and to take into account these effects on the results of the NMR experiment. In particular, the problem of IMFG becomes very difficult in cases when the applied external magnetic field gradients are not high enough.

One of the methods to avoid IMFG effects on a result is to use special pulse sequences which decrease these effects (for example, the so-called “13 interval sequence”). Nevertheless, it turns out that these sequences do not fully compensate the IMFG contribution; moreover, the mechanisms of this compensation have not yet been clarified. Another way is the detailed investigation of IMFG itself, because they reflects porous material properties. Thus, IMFG effects become very important topic to study [16–18].

The effect of internal gradients was studied by our group for a sand sample with particle size 300 − 400 μm using a stimulated spin-echo sequence, on a spectrometer operating with a superconductor magnet at $H_0 = 7$ T. The sand samples were filled with tridecane (diffusion coefficient of tridecane is $D_S = 0.68 \cdot 10^{-9}$ m^2/s). Pulsed field gradient was not applied in these experiments. The diffusion decay curves were obtained as functions of τ:

$$A(\tau) \equiv A\left(\tau, \tau_1, g_{int}^i\right) \propto \sum\nolimits_i p_i \exp\left(-\gamma^2\delta^2\left(g_{\text{int}}^i\right)^2 t_d D_s\right), \tag{2}$$

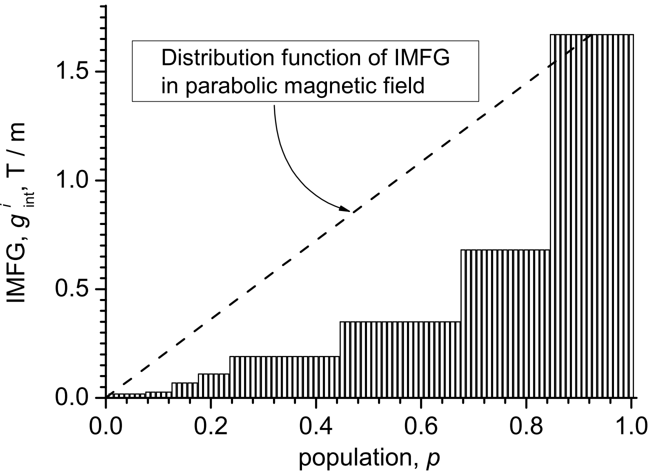

Fig. 4. Distribution function of IMFG calculated for sand sample with tridecane

where

$$\left(g^i_{\mathrm{int}}\right)^2 = \left|\operatorname{tg}\alpha^i\right|, \quad \alpha^i = \frac{\Delta \ln A(\tau)}{\Delta \ln\left(\gamma^2\delta^2 t_d D_S\right)}.$$

Fig. 3 shows the typical shape of diffusion decay $A(\tau)$ for the studied system. A family of curves was obtained for different diffusion times Δ varied from 5 to 320 ms. Each curve of the family was analyzed in accordance with Eq. (2), and the values of the internal gradients were calculated in this way. IMFG distribution function was presented as a histogram, where the column width corresponds to "population" p_i $\left(\sum p_i = 1\right)$ and the column height represents g^i_{int} value. Location of columns on histogram was chosen consecutively according g^i_{int} value. In the Fig. 4. such a histogram is shown for the sand/tridecane system at $\Delta = 80$ ms.

It should be noted that the shape of the obtained IMFG distribution differs significantly from the parabolic magnetic field, $(H(z) \propto z^2,\ g = g(z))$, which is usually used in theoretical work concerning the problem of taking into account the IMFG effect [19]. As seen in Fig. 4, the relative weight of high IMFG values is rather low (less than 20%).

Fig. 5 reveals a decrease of internal field gradients g^i_{int} with increase in Δ. This effect is conditioned by translational mobility of diffusant molecules.

According to the experimental data (Fig. 5) the maximum calculated gradient decreases from 11.6 T/m to 0.7 T/m as the diffusion time increases from 5 to 320 ms.

Thinking of the nature of the IMFG in the porous media, it is interesting also to compare $A(\tau)$ dependences for the fully and partially filled porous media. In Fig. 6 $A(\tau)$ dependences are shown for the tridecane in sand at 20% and 100% saturation of porous media. It is interesting to note, that distributions of internal field gradients are distinguished for samples with different fillings (at the same diffusion time): for the sample filled up to 20% the fraction of larger IMFG was more in comparison with the sample filled up to 100%.

Thus, the study of the internal magnetic field gradient, which was performed with stimulated spin-echo, showed that: (i) for the natural sand/tridecane system studied, the distribution of IMFG values may not be described within the framework of the parabolic field model; (ii) increase in the mean square displacement of the diffusant molecules leads to change of the internal field gradient distribution function. The maximum measured g^i_{int} value decreases due to the effect of averaging the internal field gradient by the diffusing liquid. The The relative weight of the larger IMFG values is higher for the

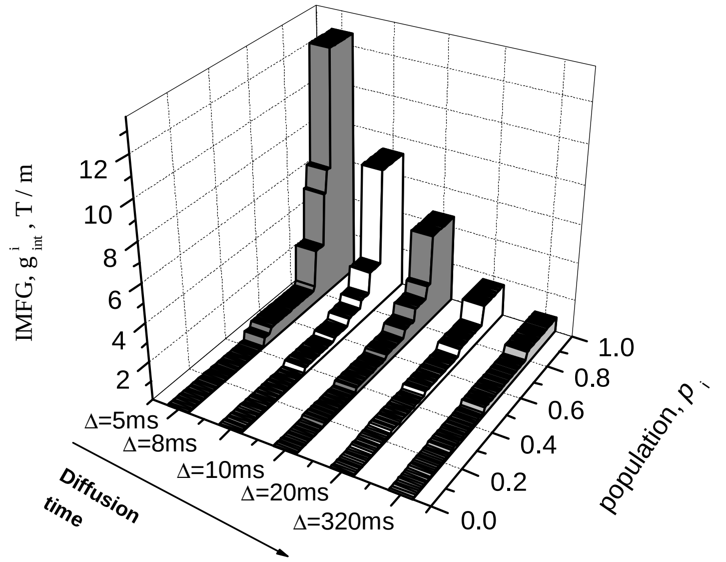

Fig. 5. Distribution function of IMFG, calculated from experimental decays

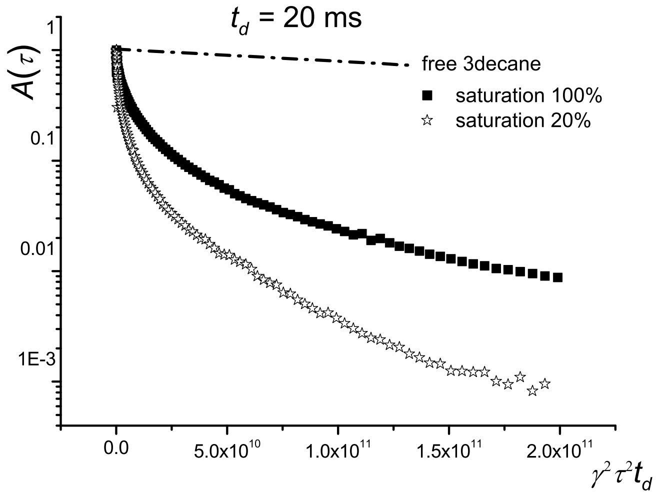

Fig. 6. $A(\tau)$-dependence, $t = 20$ ms

partially saturated porous media that gives information about localization of the fluid molecules.

Thus, IMFG studies studies believe to be very perspective in terms of obtaining information not only about porous media structure, but also about fluid localization in there.

4. Water flows through porous media

4.1. Filtration through porous media: "stagnant" areas of fluid and their characteristics. Typical technique to obtain information about such porous media characteristics as porosity and permeability is studying the flow through the porous matrix. It was found recently [20–22], that under the flow condition there are some zones

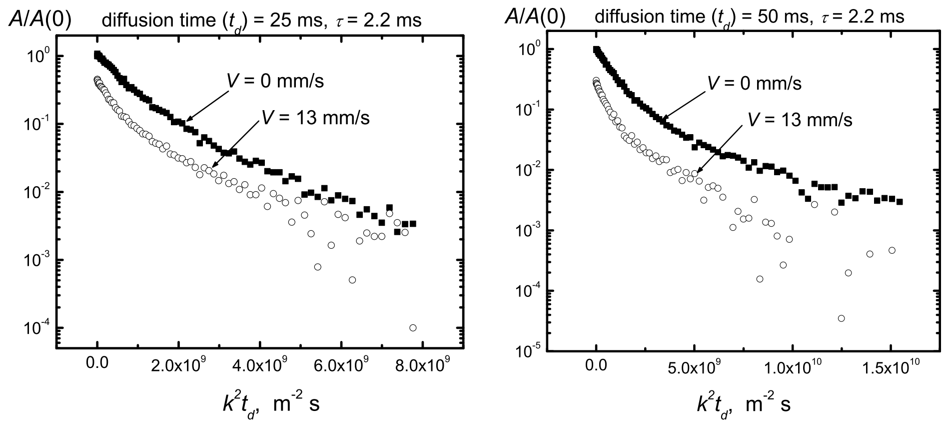

Fig. 7. Diffusion decays obtained for water molecules in sand

("stagnant" areas) in the porous matrix that are not involved in the flow. Obviously, it leads to the incorrect porosity values determination by the "flow" techniques and it is important to find the way to analyze these zones properties and their contribution to the total porosity. In a static regime (without fluid flow) it is impossible to select the contributions from liquid in stagnant zones and in closed pores from the liquid in penetrable pores by diffusion decay analysis. This can be explained by the very close values of the diffusion coefficients corresponding to these "types" of liquid. A difference in mobility can be achieved by the creation of a fluid flow inside the porous media studied. In this case one part of the liquid molecules will be involved in the flow and, thus, will be characterized by an extra (induced) diffusion coefficient. Another part of the molecules located in "stagnant" zones (including the locked pores) will be characterized by lower values of the diffusion coefficient. The detailed analysis of diffusion decays obtained for systems with fluid flow allows one to estimate the fraction of molecules located in "stagnant" zones, and, in some cases, to define the fraction corresponding to each pore type.

In order to define the characteristics of "stagnant" zones the translational mobility of the water involved in flow was studied for sands with particle size 300–400 μm. The diffusion decays obtained by the stimulated spin-echo sequence for the system without flow and with fluid flow, velocity $v = 13$ mm/s, are depicted in Fig. 7. This indicates that flow leads to two main effects: increase in the initial slope of the diffusion decays, and decrease in the initial amplitude of the spin-echo signal as compared with the amplitude at $v = 0$ mm/s.

Nevertheless, the tails of the diffusion decays have not changed. This means that some of the liquid molecules in the porous medium were not involved in the flow and, consequently, they should be attributed to so-called "stagnant" zones. The initial amplitude decrease is related to extra misphasing due to internal gradient effects. These effects increase as the diffusion time increases.

Comparing the diffusion decays obtained for samples with and without flow it is easy to obtain the fraction ($p_{\rm st}$) of molecules not changing the translational characteristics. In particular, for the sand/water system studied the fraction $p_{\rm st}$ decreases in accordance with an exponential law as the diffusion time increases (Fig. 8). This $p_{\rm st}(t_d)$ dependence shows that as the diffusion time increases most of the water molecules are involved in flow and their transport properties are sufficiently changed.

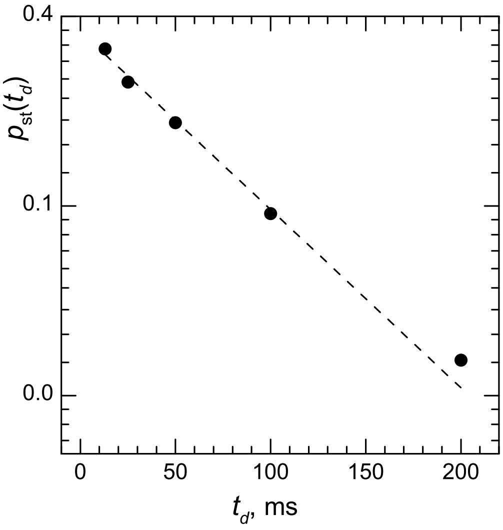

Fig. 8. Dependence of population corresponding to water not involved in flow on the diffusion time at flow velocity 13 mm/s

The molecules involved in flow can exchange with molecules located in "stagnant" zones due to self-diffusion.

Applying the approach developed to study the exchange processes, it is easy to determine the mean life-time (τ_h) of molecules in the "stagnant" zones from the data presented in Fig. 8 and the relation

$$p_{\rm st}(t_d) = p_{\rm st}(0) \cdot \exp\left(-\frac{t_d}{\tau_h}\right).$$

The calculated time (τ_h) was equal to 105 ± 5 ms; it allows one to obtain the mean size of "stagnant" zones by the Stokes – Einstein equation. The calculated value was 30 ± 3 μm, in agreement with the pore structure of sand and its particle size ($300 - 400$ μm).

5. Anomalous dynamic properties of low molecular weight liquids confined in porous media. Molecular exchange processes

In addition to the changes in translational mobility of liquids, conditioned by obstacles, in a number of papers an anomalous behavior of the self-diffusion coefficient was found [1, 23, 24]. Decrease in the concentration of liquid resulted in an increase in the molecular mobility. Sometimes measured self-diffusion coefficients exceeded D_0 by a a factor of ten or even more. A hypothesis was proposed about the fast (from the NMR point of view) exchange between the molecules of liquid and saturated vapor. As the result of a number of investigations [25, 26] and [1] we can now establish the mechanism of influence of saturated vapor on the diffusion of confined liquid as the result of fast molecular exchange between the vapor and the liquid phases. For the first time this exchange was measured experimentally by the PFG NMR technique in [1] and the form of the function for the lifetime distribution in the liquid phase was determined. It was shown that the form of this function is very sensitive to the interaction of liquid molecules with the surface. In the case of partial saturation, the surface affects the character of the liquid distribution in the porous space. From these data the need for careful preparation of the experiments is clear, as well as the analysis of experimental data itself for the self-diffusion of small-size (particularly fugitive) liquids in porous media.

For the first time, the problem of measurements of diffusion in the presence of exchange between phases was considered for an example of a two-phase system [27]. It was carried out on the basis of the assumption of exponential distribution functions of the phase lifetimes. Intermediate exchange is most interesting. For instance, diffusion decay is described by a continuous spectrum of self-diffusion coefficients even in the case of the two-phase system. The most important result [28] is that the spectrum is unambiguously bounded by D_{sa} and D_{sb} values and the component populations $p_a(t_d)$ and $p_b(t_d)$, which are decreasing functions of diffusion time t_d. To summarize, the analysis of $p_{a,b}(t_d)$ dependence provides the possibility of determining the distribution function $\psi(\tau)$ for lifetimes in phases.

The authors would like to thank Schlumberger Research & Development (RUP1-1331(3)-KA-05 project) and Federal Scientific Program (contract No 02.445.11.7017) for the support of this research.

Резюме

В.Д. Скирда, А.Р. Мутина, Р.В. Архипов. Исследования трансляционной подвижности в пористых средах методом ЯМР с импульсным градиентом магнитного поля: ограниченная диффузия, локальные магнитные поля, потоки и молекулярный обмен.

В статье рассмотрены основные принципы применения ЯМР с импульсным градиентом магнитного поля для исследования пористых систем. Показано, что исследование зависимостей коэффициента самодиффузии от времени диффузии при соответствующей обработке экспериментальных данных может дать прямую информацию о размерах ограничений. Обращено внимание на необходимость применения мощных внешних градиентов магнитного поля в связи с наводимыми в неоднородных структурах значительными внутренними градиентами магнитного поля, искажающими экспериментальные данные.

Показано, что информация о структуре пористого пространства и распределении жидкости в ней может быть в принципе получена в режиме исследования диффузионных затуханий только во внутренних градиентах магнитного поля. Для этого предложено исследовать зависимость амплитуды стимулированного эха от величины первого временного интервала в импульсной последовательности (τ-scanning) при варьируемых значениях времени диффузии. Этот эксперимент позволяет оценить значения и ширину распределения внутренних градиентов магнитного поля в исследуемой системе. В частности, показано, что в пористых системах, частично насыщенных жидкостью, по информации о внутренних градиентах магнитного поля можно судить о распределении жидкости в пористом пространстве.

К одной из актуальных проблем фильтрации жидкости через пористую среду относится задача количественной оценки так называемых застойных зон. В работе демонстрируются возможности метода ЯМР с импульсным градиентом магнитного поля для регистрации относительной доли жидкости, заключенной в такие зоны, а также определения характеристик молекулярного обмена между этой жидкостью и жидкостью, непосредственно участвующей в фильтрационном потоке.

Очень интересными и информативными могут быть результаты применения метода ЯМР с градиентом магнитного поля к исследованию процессов обмена между различными фазовыми состояниями жидкости в пористой среде. В частности, из построенных зависимостей коэффициентов самодиффузии молекул в разных фазах от времени диффузии кажущихся населенностей удается получить информацию не только о среднем времени жизни в фазе, но и о функции распределения этих времен.

Literature

1. *Valiullin R.R., Skirda V.D., Kimmich R., Stapf S.* Molecular exchange processes in partially filled porous glass as seen with NMR diffusometry // Phys. Rev. E. – 1997. – V. 55. – P. 2664–2671.

2. *Valiullin R.R., Skirda V.D.* Time dependent self-diffusion coefficient of molecules in porous media // J. Chem. Phys. – 2001. – V. 114. – P. 452–458.

3. *Fordham E.G., Gibbs S.J., Hall L.D.* Partially restricted diffusion in a permeable sandstone: Observations by stimulated echo PFG NMR // Magn. Res. Imaging. – 1994. – V. 12. – P. 279–284.

4. *Hurlimann M.D., Helmer K.G., Latour L.L., Sotak C.H.* Restricted diffusion in sedimentary rocks. Determination of surface-area-to-volume ratio and surface relaxivity // J. Magn. Reson. – 1994. – V. 111A. – P. 169–178.

5. *Latour L.L., Mitra P.P., Kleinberg R.L., Sotak C.H.* Time-dependent diffusion coefficient of fluids in porous vedia as a probe of surface-to-volume ratio // J. Magn. Reson. – 1993. – V. 101A. – P. 342–346.

6. *Mitra P.P., Sen P.N., Swartz L.M.* Short-time behavior of the diffusion coefficient as a geometrical probe of porous media // Phys. Rev. B. – 1993. – V. 47. – P. 8565–8574.

7. *Callaghan P.T.* Pulsed-gradient spin-echo NMR for planar, cylindrical, and spherical pores under conditions of wall relaxation // J. Magn. Reson. – 1994. – V. 113A. – P. 53–59.

8. *Linse P., Soderman O.* The validity of the short-gradient-pulse approximation in NMR studies of restricted Diffusion. Simulations of Molecules Diffusing between Planes, in cylinders and spheres // J. Magn. Reson. – 1995. – V. 116A. – P. 77–86.

9. *Neuman C.H.* Spin echo of spins diffusing in a bounded medium // J. Chem. Phys. – 1974. – V. 60. – P. 4508–4511.

10. *Blees M.H.* The effect of finite duration of gradient pulses on the pulsed-field-gradient NMR method for studying restricted diffusion // J. Magn. Reson. – 1994. – V. 109A. – P. 203–209.

11. *Tanner J.E.* Transient diffusion in a system partitioned by permeable barriers. Application to NMR measurements with a pulsed field gradient // J. Chem. Phys. – 1978. – V. 69. – P. 1748–1754.

12. *Balinov B., Jonsson B., Linse P., Soderman O.* The NMR self-diffusion method applied to restricted diffusion. Simulation of echo attenuation from molecules in spheres and between planes // J. Magn. Reson. – 1993. – V. 104 A. – P. 17–25.

13. *Katz A.J., Thompson A.H.* Fractal sandstone pores: implications for conductivity and pore formation // Phys. Rev. Lett. – 1985. – V. 54. – P. 1325–1328.

14. *Borgia G.C., Brown R.J.S., Fantazzini P.* Scaling of spin-echo amplitudes with frequency, diffusion coefficient, pore size, and susceptibility difference for the NMR of fluids in porous media and biological tissues // Phys. Rev. E. – 1995. – V. 51. – P. 2104–2114.

15. *Chachaty C., Korb J.-P., Van der Maarel J.-P.C., Bras W., Quinn P.* Fractal structure of a cross-linked polymer resin: a small-angle x-ray scattering, pulsed field gradient, and paramagnetic relaxation study // Phys. Rev. B. – 1991. – V. 44. – P. 4778–4793.

16. *Song Y.-Q.* Detection of the high eigenmodes of spin diffusion in porous media // Phys. Rev. Lett. – 2000. – V. 85. – P. 3878–3881.

17. *Song Y.-Q.* Using internal magnetic fields to obtain pore size distributions of porous media // Concepts in Magn. Reson. – 2003. – V. 18A. – P. 97–110.

18. *Song Y.-Q., Lisitza N.V., Allen D.F., Kenyon W.E.* Pore geometry and its geological evolution in carbonate rocks // Petrophysics. – 2002. – V. 43. – P. 420–427.

19. *Le Doussal P., Sen P.N.* Decay of nuclear magnetization by diffusion in a parabolic magnetic field: An exactly solvable model // Phys. Rev. B. – 1992. – V. 46. – P. 3465–3485.

20. *Callaghan P.T., Coy A., Macgowan D., Packer K.J.* Diffusion of fluids in porous solids probed by pulsed field gradient spin echo NMR // J. Molec. Liq. – 1992. – V. 54. – P. 215–228.

21. *Seymour J.D., Callaghan P.T.* Generalized approach to NMR analysis of flow and dispersion in porous media // J. of AIChE. – 1997. – V. 43. – P. 2096–2111.

22. *Callaghan P.T., Codd S.L., Seymour J.D.* Spatial coherence phenomena arising from translational spin motion in gradient spin echo experiments // Concepts Magn. Reson. – 1999. – V. 11. – P. 181–202.

23. *Dvoyashkin N.K., Skirda V.D., Maklakov A.I., Belousova M.V., Valiullin R.R.* Peculiarities of self-diffusion of Alkane molecules in Kaolinite // Appl. Magn. Reson. – 1991. – V. 2, No 1 – P. 83–91.

24. *Orazio F.D., Bhattacharja S., Halperin W.P.* Enhanced self-diffusion of water in restricted geometry // Phys. Rev. Lett. – 1989. – V. 63. – P. 43–46.

25. *Maklakov A.I., Dvoyashkin N.K., Khozina E.V., Skirda V.D.* Temperature dependence of tridecane self-diffusion coefficient in porous media // Colloid J. of Colloid and Polymer Science. – 1995. – V. 55, No 1. – P. 55–60.

26. *Maklakov A.I., Dvoyashkin N.K., Khozina E.V.* New "gas-like" state of liquid in porous media // Colloid J. of Colloid and Polymer Science. – 1993. – V. 55. – P. 79–83.

27. *Karger J.* Zur massbarkeit von diffusionkoeffizienten in zweiphase system mit hilfe der methode der gepulsten feldgradienten // Annalen der Physik. – 1969. – V. 24, No 1–2. – P. 1–7.

28. *Maklakov A.I., Skirda V.D., Fatkullin N.F.* Self-diffusion in polymer systems, in encyclopedia of fluid mechanics / Ed. N. Cheremisinoff. – Houston: Gulf Publ.Co., 1990. – 705 p.

Поступила в редакцию
13.10.05

Скирда Владимир Дмитриевич – доктор физико-математических наук, профессор, заведующий кафедрой молекулярной физики Казанского государственного университета.

E-mail: *vskirda@ksu.ru*

Мутина Альбина Ришатовна – аспирант кафедры молекулярной физики Казанского государственного университета.

E-mail: *amutina@ksu.ru*

Архипов Руслан Викторович – младший научный сотрудник кафедры молекулярной физики Казанского государственного университета.

E-mail: *rarchipo@ksu.ru*