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Molecular exchange processes in partially filled porous glass as seen with NMR diffusometry

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The self-diffusion properties of hexane confined in porous glass with different filling fractions were studied by means of pulsed field-gradient spin echo diffusometry. The spin echo attenuation curves were analyzed over a range of 3.5 orders of magnitude. Only for the partially filled sample was the shape of the echo attenuation curves found to depend on diffusion time. This observation indicates a vapor phase contribution to the total diffusional displacements and is interpreted by molecular exchange between the liquid and vapor phases. The distribution of molecular residence times in the liquid phase is evaluated from experimental data. A thorough analysis of this distribution function yields information about the nature of inhomogeneities of the liquid's spatial distribution inside the porous matrix, including typical sizes of the inhomogeneous regions and characteristics of exchange processes at the liquid/vapor interface. The model is further substantiated by additional computer simulations. [S1063-651X(97)02202-2]

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I. INTRODUCTION

Investigations of the time dependence of the self-diffusion coefficient $D(t)$ for liquids confined in porous media have recently become a widely used approach to characterize the structure of porous materials. A favorable method employed for this purpose is pulsed field-gradient spin echo (PGSE) diffusometry [1,2]. It was shown that $D(t)$ can be related to certain characteristics of the porous medium such as the surface-to-volume ratio and the tortuosity [3,4]. Taking into account merely geometrical restrictions of the medium, $D(t)$ of a diffusing fluid is found to decrease with time and finally to attain a plateau value. Following a more general approach that describes the motion of particles in a random force field, as induced by a heterogeneous medium, qualitatively yields the same results [5]. The presence of a restricting geometry therefore results in a reduction of the self-diffusion coefficient of the intraporous liquid compared to the bulk value.

However, in some cases self-diffusion coefficients of liquids in porous materials were found to exceed those of the bulk liquids [6–11]. One possible explanation can be fast (relative to the NMR time scale) exchange of molecules between the two phases of liquid and saturated vapor. An attempt to prove experimentally the influence of vapor diffusion was undertaken in [9], using sample compression, i.e., the reduction of space available for the vapor phase. For high compressions, the measured values of the self-diffusion coefficient were bulklike, while for large fractions of vapor-filled volume they were found to exceed the bulk values. Corresponding effects were observed at increasing the liquid's molecular mass or decreasing the temperature as well as decreasing the specific surface of the porous medium [11]. In the latter cases the occurrence of bulklike self-diffusion coefficients in partially filled samples was attributed to slow exchange. The exchange process itself, on the other hand, could not be detected until now in the samples under investigation, though methodological aspects of the study of molecular exchange processes during self-diffusion were described in detail [12,13].

The aim of the present work is to study the properties of interface molecular exchange in partially saturated porous media for the example of the system hexane/Bioran porous glass employing experimental results for translational diffusivity.

II. METHOD AND SAMPLES

In a conventional PGSE [14] experiment [see Fig. 1(a)], the amplitude of the stimulated echo at time $2\tau_1+\tau_2$ is observed for different values of the wave number $k=\gamma\delta g$, where γ denotes the gyromagnetic ratio; δ and g are the width and strength of the field-gradient pulses in between the $\pi/2$ radio-frequency (rf) pulses.

If the linear Einstein relationship of the mean square displacement of the spin-bearing particles,

$$\langle r^2(t)\rangle = 6Dt, \tag{1}$$

is fulfilled (where D is the isotropic diffusion coefficient of the liquid), the intensity of the stimulated echo $A(2\tau_1+\tau_2)$ is related to the initial signal intensity $A(0)$ following the first rf pulse by

$$\frac{A(k^2)}{A(0)} = \frac{1}{2}\exp\left[-Dk^2\left(\Delta-\frac{\delta}{3}\right)\right]\exp\left(-\frac{2\tau_1}{T_2}\right)\times\exp\left(-\frac{\tau_2}{T_1}\right). \tag{2}$$

T_1 and T_2 are the longitudinal and transverse relaxation times of the spin system, respectively. For an experiment with all times fixed but only the gradient strength g varied, relaxation leads to a constant attenuation factor and need not be taken into account in the analysis. The stimulated echo sequence [Fig. 1(a)] has been modified for our purposes by

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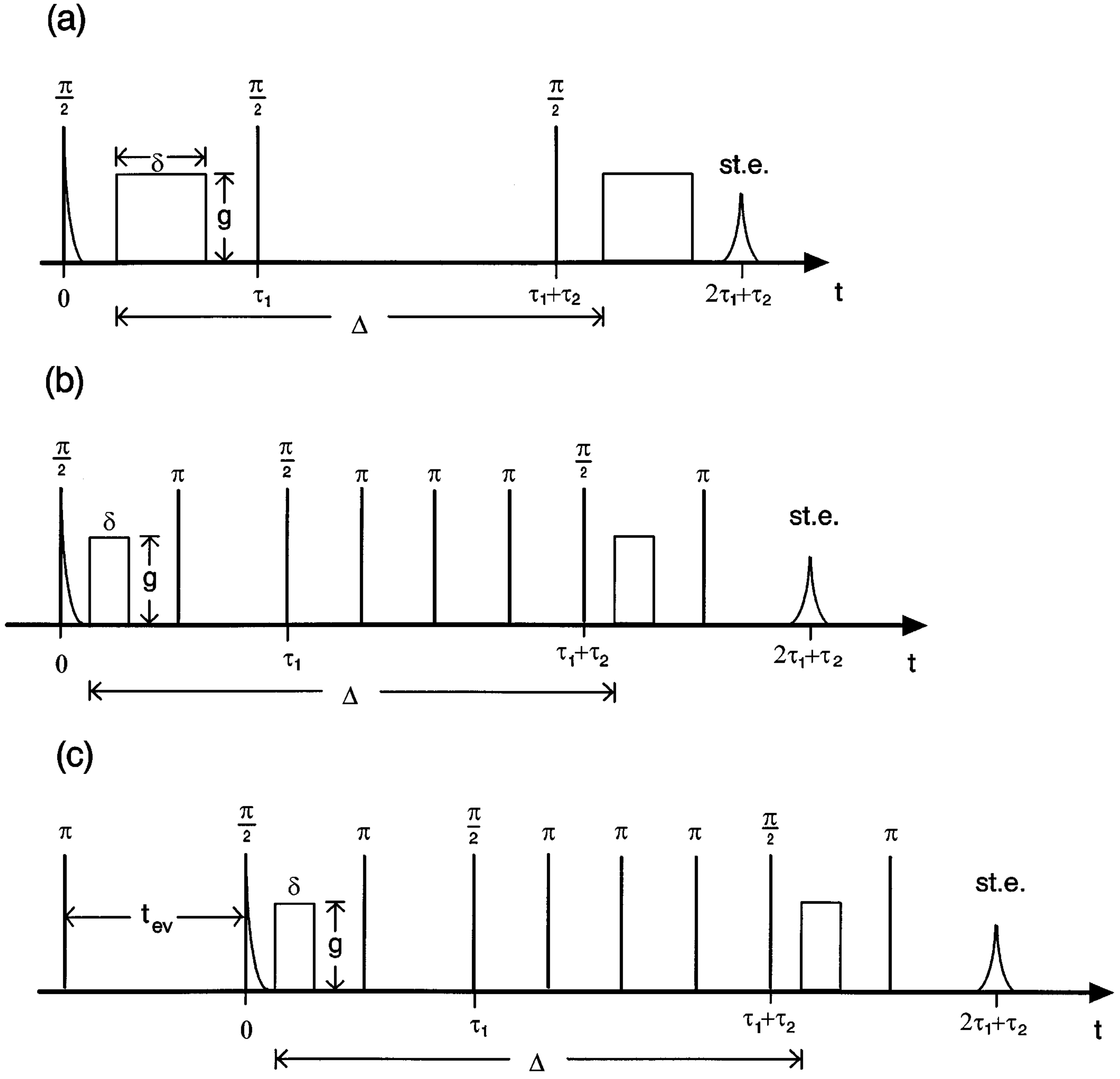


FIG. 1. Radio-frequency pulse sequences for diffusion experiments. (a) Stimulated echo sequence with gradient pulses of strength g and duration δ; the intensity of the stimulated echo (st.e.) at time $2\tau_1+\tau_2$ is determined as a function of g. (b) Modification for suppression of the effects of intrinsic magnetic field gradients. (c) Modification for investigating the presence of relaxation effects on diffusion measurements.

adding a train of π pulses during the interval between the second and third $\pi/2$ pulses [Fig. 1(b)] in order to exclude a possible influence of internal magnetic field gradients which may become essential in highly dispersed systems [15]. In a second variant, another π pulse was applied preceding this pulse sequence for the investigation of relaxation effects on the diffusional behavior by variation of the evolution interval t_{ev} [Fig. 1(c)].

All experiments were carried out on a home-built PGSE spectrometer with a maximum field gradient of 106 Tm^{-1} operating at a proton resonance frequency of 64 MHz. The duration of the gradient pulses, δ, was chosen between 10 and 30 μs, the diffusion time $t_d=\Delta-\delta/3$ was varied from 3 to 1500 ms, and the interval τ_1 between the first and the second $\pi/2$ rf pulses from 1.4 to 2.4 ms. All measurements were carried out at a temperature of (30 ± 0.5) °C. As a suitable medium, Bioran porous glass was purchased from Schott Glaswerke, Mainz, Germany. The material forms spongelike macroparticles of 80–130 μm diameter with a porosity of $(74\pm3)\%$ and a specific surface of 120 m^2/g. The pore-size distribution is specified to be narrow with ca. 95% of the pores having diameters of (40 ± 4) nm. From previous investigations we conclude a porous structure with randomly formed channels of 40 nm diameter and an average

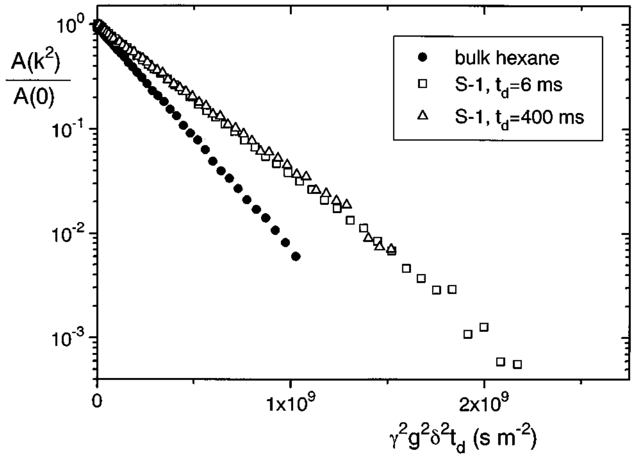


FIG. 2. Diffusional decays (DDs) obtained for bulk hexane and sample S-1 for different diffusion times t_d. The quantities given on the abscissa are the gradient pulse intensity g and duration δ, the gyromagnetic ratio γ and the diffusion time t_d, respectively.

radius of the percolation cycle — defining the length scale on which diffusion obeys a Gaussian propagator — of about 1 μm [16].

The glass material was heated to 200 °C under vacuum for 24 h and filled with hexane (Fluka Chemica, Buchs, Switzerland, 99.5% pure) under vacuum by the bulk-to-bulk method. Two samples with ratios of liquid volume to pore volume of 1 and 0.66, respectively, were studied. They will be denoted as S-1 and S-0.66.

III. EXPERIMENT

The experimental diffusional decays (DDs) for different diffusion times t_d are shown in Figs. 2 and 3. As the data in Fig. 2 imply, the DDs of bulk hexane and of the completely filled porous sample S-1 are monoexponential and do not depend on diffusion time. The self-diffusion coefficients are evaluated as $D_{\mathrm{bulk}}=(4.90\pm0.25)\times10^{-9}$ m^2 s^{-1} and $D_{S\text{-}1}=(3.35\pm0.15)\times10^{-9}$ m^2 s^{-1}, respectively. Contrary to this finding, the DDs of the partially filled sample S-0.66 are nonexponential, and their shape depends strongly on the diffusion time (Fig. 3). The initial parts of the DDs are characterized by a self-diffusion coefficient more than twice as large as in the bulk liquid and independent of diffusion time within the experimental errors. Such a DD function may occur due to either a nonexponential character of the longitudinal relaxation or a multiphase structure of the system in which the exchange process takes place [12,17]. In order to investigate the first possible effect, a stimulated-echo pulse sequence preceded by a π pulse was applied [see Fig. 1(c)]. For longitudinal relaxation recovery times t_{ev} between 10 ms and 10 s, all obtained DDs were found to coincide. One may therefore conclude that the observed nonexponentiality of the DDs and their dependence on diffusion time might be connected with an exchange process between phases that can be characterized by different translational mobilities. This assumption is in agreement with the above-mentioned independence of the initial slope on diffusion time [12].

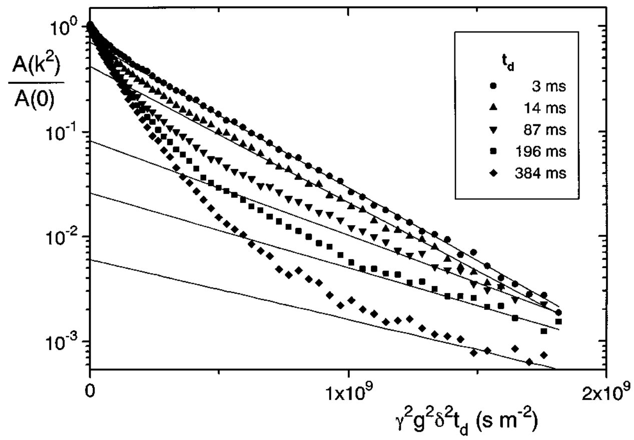


FIG. 3. Diffusional decays (DDs) obtained for the sample S-0.66 for different diffusion times t_d. Solid lines are tangents to the final section of the curves.

IV. INFLUENCE OF EXCHANGE PROCESSES ON NMR SELF-DIFFUSION EXPERIMENTS

The problem of NMR self-diffusion measurements in the presence of exchange between phases of different properties was first discussed by Kärger [13] for the special example of a two-phase system with an exponential molecular lifetime distribution function. The solution obtained by the author is essentially a simple transference of conclusions found for the analogous problem of nuclear magnetic relaxation in a multiphase system [18] and suggests the evaluation of the self-diffusion coefficient as a function of diffusion time. Thus, a correction for nuclear relaxation during the diffusion period cannot be applied. Furthermore, the *a priori* assumption of an exponential lifetime distribution makes Kärger's approach [13] unsuitable for the study of more complex systems.

A solution for the problem of general lifetime distributions is given in [17]. Here, the spin-echo amplitude is recorded solely as a function of the strength of the magnetic field gradient pulses, while the relevant times can be varied between experiments to account for relaxational effects.

We will restrict ourselves to a system with two phases A, B with lifetimes t_A, t_B. In this case, two limiting conditions can be distinguished for which simple solutions exist: If the fast-exchange condition applies ($t_d \gg t_A, t_B$), an average diffusion constant D_S is observed which can be expressed by

$$D_S = p_A D_A + p_B D_B, \tag{3}$$

where p_i is the population of phase i with self-diffusion coefficient D_i. In the opposite limit of slow exchange ($t_d \ll t_A, t_B$), the diffusional decay can be decomposed into a sum of two exponentials:

$$\frac{A(k^2)}{A(0)} = p_A \exp[-k^2 t_d D_A] + p_B \exp[-k^2 t_d D_B]. \tag{4}$$

In cases where these limits do not apply, the diffusional decay has to be described by a more general expression according to [17]:

$$\frac{A(k^2)}{A(0)}=\sum_j W_j(t_{Aj},t_{Bj})\exp[-k^2(D_A t_{Aj}+D_B t_{Bj})], \qquad (5)$$

where t_{Aj} and t_{Bj} are the total lifetimes of a nucleus in the phases with the self-diffusion coefficients D_A and D_B, respectively ($t_d=t_{Aj}+t_{Bj}$). $W_j(t_{Aj},t_{Bj})$ is the corresponding probability for a certain pair of lifetimes t_{Aj} and t_{Bj}. Thus, the diffusional decay can be described formally by a quasi-continuous spectrum of apparent self-diffusion coefficients $D_j=(D_A t_{Aj}+D_B t_{Bj})\ t_d^{-1}$. If one or both of the limiting values of this spectrum, D_A and D_B, can be extracted from the experimental data or are known beforehand, information about the nature of the exchange process taking place and the relevant lifetimes can be obtained by analyzing the distribution of the components in $A(k^2)$.

It was shown in [17] that the probability $p_i(t_d)$ for a particle of not having left phase i during an interval t_d can be written as

$$\frac{p_i(t_d)}{p_i(0)}=1-\int_0^{t_d}\psi_i(\tau)\ d\tau, \qquad (6)$$

where $p_i(0)$ is the fraction of particles in phase i. $\psi_i(\tau)$ represents the normalized lifetime distribution function in phase i; thus the integral on the right-hand side describes the probability of a particle having left phase i during t_d. It should therefore be possible to derive the lifetime distribution function $\psi_i(\tau)$ by analyzing the experimentally obtained diffusional decay curves. This procedure is simplified by knowing the smallest D value, which will be discussed in the following section.

V. ANALYSIS AND DISCUSSION OF EXPERIMENTAL RESULTS

In order to find a description of the lifetime distribution function $\psi(\tau)$, we shall consider the behavior of the smallest component D_{min} and its relative population. Figures 4 and 5 show the dependence of D_{min} and its population p_{min} as a function of diffusion time t_d for the samples S-1 and S-0.66. The value of D_{min} is defined by the tangent of the final part of the DD curves. During the fitting procedure it was made sure that, after subtracting the diffusional decay corresponding to the smallest component, the residual DD did not depend on diffusion time. Employing this method, both D_{min} and p_{min} could be evaluated with reasonable accuracy in the described range of diffusion times. However, it must be pointed out that great care generally has to be taken for the interpretation of nonexponential or multiexponential decay curves. In our case, where only the asymptotic values have been of interest, the analysis was restricted to diffusion times where D_{min} could still be defined unambiguously despite decreasing signal-to-noise ratios.

A single self-diffusion coefficient was found in the case of completely filled pores (sample S-1). For the shortest diffusion time in the experiments, $t_d=3$ ms, the average displacement is already on the order of 10^{-5} m, exceeding both the pore diameter and the radius of the percolation cycle [16]. One therefore expects [4,5] a diffusion coefficient reduced compared to the bulk value D_{bulk} but independent of diffusion time, as was observed (Fig. 4). The ratio of the self-diffusion coefficients, $D_{S\text{-}1}/D_{\text{bulk}}\approx 0.7$, is in agreement with findings for analogous systems published in a previous work [19]. The obtained results (Fig. 5) do not indicate, within experimental errors, the presence of a second component in the whole range of diffusion times. This implies that, according to Eq. (4), no exchange is observed for sample S-1 in the range 3 ms$\leqslant t_d \leqslant$1500 ms.

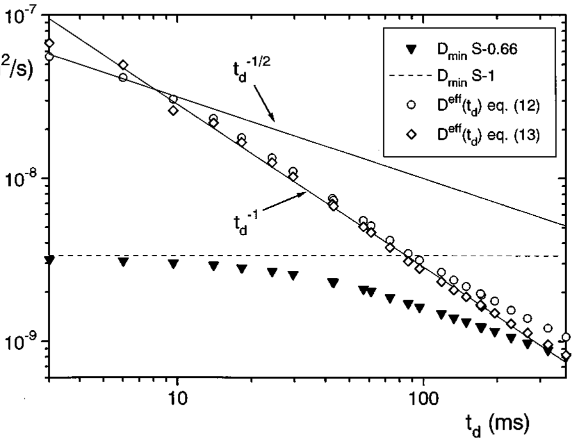


FIG. 4. Smallest self-diffusion coefficients $D_{\text{min}}\equiv D_A$ obtained from tangents to the final sections of the diffusional decays. Experimental data for the samples S-1 and S-0.66 (dashed line and solid triangles) and effective self-diffusion coefficients $D^{eff}(t_d)$ calculated with Eq. (12) (circles) and Eq. (13) (diamonds), respectively. Solid lines indicate power-law relations for comparison.

For the partially filled sample S-0.66, on the other hand, the relative contribution of the smallest component D_{min} depends strongly on diffusion time, indicating the presence of an exchange process. In addition to that, the value of D_{min} itself decreases for diffusion times longer than about 20 ms, which can be understood as a consequence of the onset of spatial restriction. The fact that the D_{min} values for both samples are very similar for short diffusion times leads to the conclusion that it can be attributed to the liquid phase in S-0.66. We will use the subscript A for this phase in future,

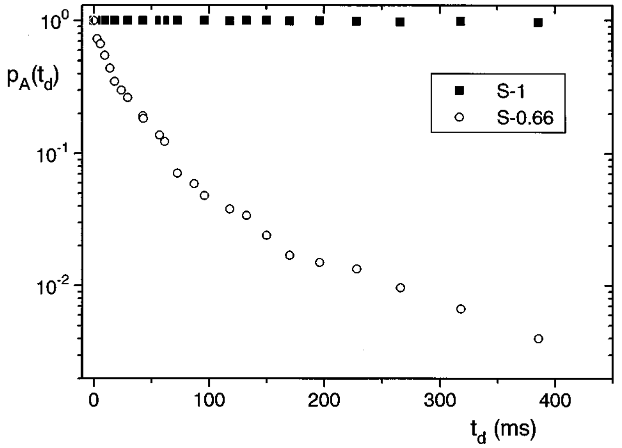


FIG. 5. Experimentally determined population $p_{\text{min}}\equiv p_A$ of the component D_{min} for the samples S-1 and S-0.66 as a function of diffusion time t_d. Phase A is equivalent to molecules in the liquid phase.

thus $D_A \equiv D_{\min}$. The dependence of D_A indicates that the liquid phase A is spatially restricted. This fact is an important peculiarity of the studied process of multiphase exchange in the sample under consideration, unlike the notion in [12,13,17].

The restriction effect is directly connected with the time dependence of the mean-square displacement. In analogy to the behavior expected for diffusion on percolation clusters, we make the ansatz

$$\langle r^2(t_d)\rangle \propto t_d^{1-\varepsilon}. \tag{7}$$

$\varepsilon = 0$ describes the case of free diffusion, while for $\varepsilon = 1$ completely restricted diffusion is observed [12]. For any value $0 \leqslant \varepsilon \leqslant 1$, an effective self-diffusion coefficient can be defined which follows the relation

$$D^{eff}(t_d) \propto t_d^{-\varepsilon}. \tag{8}$$

In particular, $D^{eff}(t_d) \propto t_d^{-1}$ indicates the regime of completely restricted diffusion. In a real physical system, both cases might be observed, i.e., $D_0 \propto t_d^0$ for short diffusion times in absence of the restriction effect and $D^{eff}(t_d) \propto t_d^{-\varepsilon}$ for longer t_d. From the experimental data in Fig. 4, only D_0 for short t_d can be extracted directly. They do not allow one to estimate $D^{eff}(t_d)$ from the asymptotic limit of $D(t_d)$ (see, e.g., [20]). To derive the long-time behavior, some simple scaling arguments have to be considered.

Let us assume that the measured value $D(t_d)$ is a function of only two parameters D_0 and $D^{eff}(t_d)$, respectively:

$$D(t_d) = f[D_0, D^{eff}(t_d)]. \tag{9}$$

Moreover, $f[D_0, D^{eff}(t_d)]$ must satisfy the following obvious limiting conditions:

$$\lim_{t_d \to 0} f[D_0, D^{eff}(t_d)] = D_0,$$

$$\lim_{t_d \to \infty} f[D_0, D^{eff}(t_d)] = D^{eff}(t_d), \tag{10}$$

where the limit $t_d \to \infty$ has to be understood as only allowing for displacements not exceeding the sample dimensions. Taking into account Eq. (8), a suitable expression fulfilling Eq. (10) is found to be

$$f[D_0, D^{eff}(t_d)] = \frac{D_0 D^{eff}(t_d)}{D_0 + D^{eff}(t_d)} = D(t_d). \tag{11}$$

Hence,

$$D^{eff}(t_d) = \frac{D_0 D(t_d)}{D_0 - D(t_d)}. \tag{12}$$

It should be noted that the behavior of $[D_0 - D(t_d)]^{-1}$ is discussed in [3,5] in order to estimate the factor connected with the restriction effect. It coincides with Eq. (12) as far as the factor $D_0\ D(t_d)$ is concerned, but its application range is limited due to the obvious violation of the conditions (10). Note that relation (12) is essentially a renormalization of $D(t_d)$ and is always valid for the description of a restriction effect, provided that the exponent ε in Eq. (8) is a function of t_d.

Equation (12) can be used to describe the data for the partially filled sample (solid triangles in Fig. 4). If $D_{S\text{-}1} = 3.35 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$ is taken as D_0, we assume that the small-scale inhomogeneities given by the porous network itself are already averaged out and that restrictions on a larger scale are under investigation. The result is marked by open circles in Fig. 4: For short diffusion times, the values of $D_A^{eff}(t_d)$ are consistent with a power law $t_d^{-1/2}$, as was predicted by theory [3,5]. For a wide range of diffusion times, $10\ \mathrm{ms} \leqslant t_d \leqslant 100\ \mathrm{ms}$, a dependence $D_A^{eff}(t_d) \propto t_d^{-1}$ is observed, which corresponds to the case of completely restricted diffusion. For diffusion times larger than approximately 100 ms, a weaker dependence of $D_A^{eff}(t_d)$ on t_d is found. We suppose this to be a result of connections within spatially restricted regions or a permeability effect which is usually characterized by $D^p = \lim_{t_d \to \infty} D^{eff}(t_d)$.

In order to take into account this effect, the value $D(t_d) - D^p$ has been discussed in [4,5] to describe the $D_A^{eff}(t_d)$ dependence. For a more precise analysis we introduce the function $\varphi(t_d) = \kappa[D(t_d) - D^p]$, where κ is defined by the condition $\lim_{t_d \to 0} \varphi(t_d) = D_0$. In conjunction with $\lim_{t_d \to 0} D(t_d) = D_0$, we eventually obtain an expression for $\varphi(t_d)$, characterizing diffusion in a medium with restrictions, corrected for permeability effects:

$$\varphi(t_d) = [D(t_d) - D^p] \frac{D_0}{D_0 - D^p}. \tag{13}$$

By substituting $\varphi(t_d)$ instead of $D(t_d)$ into Eq. (12) and fitting D^p, we find that $D_A^{eff}(t_d) \propto t_d^{-1}$ holds for $D^p = 1.8 \times 10^{-10}\ \mathrm{m^2\ s^{-1}}$ in the whole range of the studied diffusion times (open diamonds in Fig. 4), excluding the region of small t_d mentioned above. Since $D^{eff}(t_d) = \langle r^2(t_d)\rangle / 6t_d$ by definition, the restriction size $\sqrt{\langle r^2(t_d)\rangle}$ in the studied case can be calculated to equal 40 μm. The same result is obtained when the influence of D^p is neglected by considering $D_A^{eff}(t_d)$ only in the range $10\ \mathrm{ms} \leqslant t_d \leqslant 100\ \mathrm{ms}$.

This analysis of the experimental data leads to a first conclusion concerning the liquid state in the sample S-0.66: Phase A, characterized by the minimal self-diffusion coefficient value from the observed DD curve and representing hexane molecules in the liquid state, is distributed inside the sample volume in regions with a characteristic dimension of 40 μm. These regions are connected by paths that provide a permeability coefficient $\kappa_p = D^p / D_{S\text{-}1} \approx 0.05$.

As was already mentioned, the decrease of $p_A(t_d)$ with increasing t_d indicates exchange of phase A with another phase B, the properties of which can be estimated: Extrapolation of $p_A(t_d)$ for $\lim_{t_d \to 0}$ yields $1 - p_A(0) = p_B(0) \leqslant 0.01$. According to Eq. (3), the self-diffusion coefficient of the second phase must then be at least $D_B = [D_S - p_A(0) D_{(S\text{-}1)}] / p_B(0) \geqslant 9 \times 10^{-7}\ \mathrm{m^2\ s^{-1}}$. This rough estimate leads to the conclusion that a fraction of the hexane molecules is in the saturated vapor state. In this state, the bulk diffusivity of the molecules is more than three orders of magnitude larger than in the liquid, while the population in that phase is approximately proportional to the ratio of the densities of saturated vapor and liquid, resulting in a fraction of about 10^{-3}.

Let us now consider the principal experimental finding, the time dependence of $p_A(t_d)$. To a first approximation, the process of exchange between two phases A and B can be described by diffusion inside the volume of phase A to the interface [17]. This is similar to the problem of reaching the surface [21] assuming that the probability of withdrawal from the liquid phase for a molecule at the interface is close to unity. The distribution function of the lifetime in the liquid phase, $\psi_A(\tau)$, can then be written for the one-dimensional case [22] as

$$\psi_A(\tau)=(2\pi D\tau^3)^{-1/2}\left\{\frac{2D\tau}{R}\left(1-\exp\left[-\frac{R^2}{2D\tau}\right]\right)+R\ \exp\left[-\frac{R^2}{2D\tau}\right]\right\}. \tag{14}$$

Here R denotes the linear dimension of the liquid phase and D is the bulk diffusion coefficient.

For the case discussed in this work, phase B is saturated vapor. Consequently, it is not justified to consider the probability of withdrawal from the liquid phase, P_{LG}, to be equal to 1. From general considerations this probability can be approximated by the ratio of the densities of the two phases; therefore, $P_{LG}\approx 10^{-3}$.

A successful approach to describe the evolution of the population in phase A has to take into account the fraction of molecules that fail to withdraw into phase B. This can be achieved by rewriting Eq. (6) in the form

$$p_A(t_d)=1-\int_0^{t_d}\psi_A(\tau)\ d\tau+(1-P_{LG})^{\nu t_d}\int_0^{t_d}\psi_A(\tau)\ d\tau, \tag{15}$$

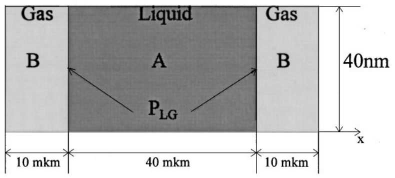
where ν is the frequency of collisions with the interface and $p_A(0)$ was approximated to unity. Employing $P_{LG}\ll 1$, Eq. (15) is simplified to

$$p_A(t_d)=1-(1-\exp[-\nu P_{LG}t_d])\int_0^{t_d}\psi_A(\tau)\ d\tau. \tag{16}$$

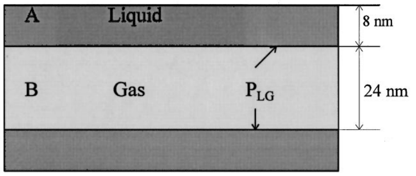
Equation (16) implies that the function $p_A(t_d)$ is determined by the process of particles diffusing to the interface only for times shorter than an average time for reaching the interface, $\overline{\tau}$, while for larger times, $p_A(t_d)$ is dominated by the exponential factor $(\nu P_{LG})^{-1}$. Note that the frequency of collisions with the phase interface, $\nu=\tau^{-1}$, is determined by the surface-to-volume ratio of the phase. The average time of reaching the surface in a phase with spherical boundaries was shown to be [21]

$$\overline{\tau}=\frac{3}{5D}\left(\frac{V}{S}\right)^2, \tag{17}$$

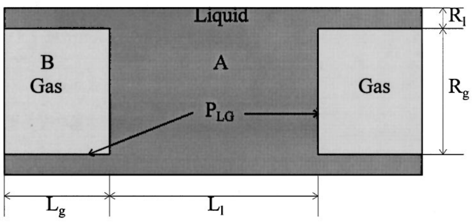
where V and S are the volume and the surface area of the phase, respectively. In our case, where the dimension of the liquid phase was estimated to 40 μm, an average time of $\overline{\tau}\approx 8$ ms is found. Consequently, under the conditions of our experiment ($3\text{ ms}\leq t_d\leq 1500\text{ ms}$), the withdrawal of the molecules from the liquid phase is defined mainly by P_{LG}, and according to Eq. (16) one can expect an exponential form of $p_A(t_d)$. From the mentioned estimations a time constant $(\nu P_{LG})^{-1}$ of the order of 10 s is obtained which is obviously much too large to coincide with the time dependence of p_A; see Fig. 5. Assuming that the order of P_{LG} is correct, a significantly smaller value for $(\nu P_{LG})^{-1}$ can only be attained by increasing the surface-to-volume ratio while the characteristic dimensions of the restrictions must be kept constant. We suggest the following picture that satisfies all these requirements: within a region with a typical size of 40 μm, A represents a continuous liquid phase where pores are filled completely, connected by narrow channels along the glass surface. Thus, the effective interface area between phases A and B becomes larger. This conclusion is similar to models proposed for nuclear magnetic relaxation studies in comparable samples (see, e.g., [23]).



a) Model M1.



b) Model M2.



c) Model M3.

FIG. 6. Graphic representation of the models used for computer simulations using the algorithm described in the text. (a) Spatial domains of phases A and B alternating along a channel; (b) liquid phase A spread along the channel surface; (c) combination of (a) and (b).

To prove the applicability of this model, a series of computer simulations was carried out. First, two limiting cases of liquid-vapor distribution in the sample were compared: (a) spatial domains of phases A and B alternating along a channel [Fig. 6(a)]; (b) the liquid phase A is spread along the channel surface [Fig. 6(b)]. This resembles a simplified view for the cases of nonwetting and wetting fluids, respectively. For the calculations, the characteristic sizes and the filling fraction have been chosen in accordance with the sample properties and (for the first model) the experimental data for

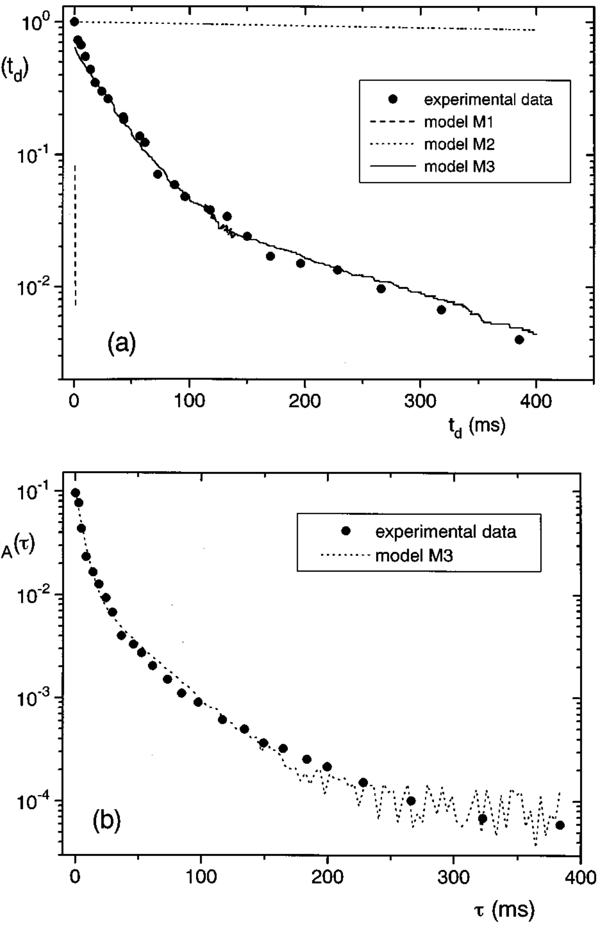


FIG. 7. Results obtained by two-dimensional computer simulation of 5000 particles performing 50 000 random steps each. Circles represent experimental results (sample S-0.66) for comparison. (a) Probability function $p_A(t_d)$; (b) lifetime distribution function $\psi_A(t_d)$.

the size of the liquid phase. The simulation of the diffusion process was performed employing the following algorithm: a random walk in two dimensions was implemented starting at an arbitrary position inside the liquid phase A which contained a uniform distribution of particles. When reaching the interface, the particle was permitted to enter the vapor phase B with the probability $P_{LG}=10^{-3}$; the step length for the random walk in phase B was 1000 times larger than in phase A, corresponding to the ratio of self-diffusion coefficients. The simulation was averaged for 5000 particles performing 50 000 random steps each. The evaluated quantities were the fraction of molecules that did not leave phase A during the simulation time t and the average self-diffusion coefficient, calculated as the ratio of the mean-square displacement to t. The results of the simulation for $p_A(t)$ are shown in Fig. 7(a).

It must be noted first that for both models, exponential forms for the function $p_A(t_d)$ were found. This implies that, due to the small value of P_{LG}, diffusion through the liquid phase towards the interface is not the limiting factor for the exchange process. The difference between the exchange rates for the two limiting models, calculated to be 3 s and 20 μs, respectively, is striking. It becomes obvious that this feature is a consequence of the two surface-to-volume ratios that differ by several orders of magnitude. In addition, only for the first model is restricted diffusion indicated for molecules that never left phase A, as was observed in the experiment. The effect of the phase distribution on the average self-diffusion coefficient behavior seems to be essential as well. The calculated value of the average self-diffusion coefficient for the second model is up to three times larger than the bulk value, while for the first model no significant difference was found, despite the fact that the total gas phase volume was the same for both models. This interesting observation can be explained by the fact that the gas phase regions in the first model are too small to allow a detectably increased mean-square displacement of the diffusing particles. The finding implies an important conclusion: in order to observe self-diffusion coefficients exceeding the bulk values significantly, not only the fast-exchange condition at the liquid-vapor interface has to be satisfied but also the domains of saturated vapor must be spread sufficiently into the pore space.

The simulations show that each of the models (a) and (b) can only describe part of the experimental results. Therefore, a combination of these models was chosen consisting of domains with dimensions denoted in Fig. 6(c). The simulation was in best agreement with the experimental data for the following set of parameters: $R_l=10$ nm, $R_g=20$ nm, $L_l=20$ μm, $L_g=20$ μm. Figure 7(a) shows the result of the simulation as a solid line compared to the experimentally determined values; in Fig. 7(b), the lifetime distribution function for the liquid phase, $\psi_A(t)$, is calculated from $p_A(t)$. During the simulation procedure, L_l was allowed to vary according to a Gaussian distribution with $\sigma=0.1$. Thus, the computer simulations confirm the picture concerning the distribution of the liquid state in partially filled samples that was made on the basis of experimental observations.

It must be noted that the character of the distribution is not exclusively determined by the morphological peculiarities of the porous glass. Our additional experiments show a strong dependence of exchange processes on temperature, filling fraction, and type of liquid. Further investigations will thus have to be performed to gain a complete understanding of all relevant processes of fluid behavior in porous glasses.

In conclusion, it should be mentioned that the complicated shape of the experimental dependence of $p_A(t_d)$ is not necessarily connected with a three-dimensional character of the liquid phase's spatial distribution [22]. Our investigations of molecular exchange between liquid and vapor phases show that the small value of P_{LG} results in an exponential form of $p_A(t_d)$ even for rather large dimensions of phase A. As a result, the polyexponential shape of $p_A(t_d)$ is due to a distribution of the domain sizes of this phase and the properties of their connections.

VI. CONCLUSIONS

The properties of translational self-diffusion in a liquid partially filling the pore space of porous glass particles was investigated using the NMR pulsed field-gradient method. The dependence of the diffusional decay shapes on diffusion time can be described by a process of molecular exchange between liquid and vapor phases. The distribution function of the molecular lifetimes in the liquid phase was, to our knowledge, derived for the first time from experimental data and can be characterized by exponential components determined by the geometry of the liquid distribution in the porous medium and diffusional exchange between both phases. The analysis of the diffusional decays as a function of the diffusion time allows estimating the characteristic size of the liquid phase domains. The properties of the liquid-vapor interface can account for the observation of restricted-diffusion effects in the liquid phase. The investigations carried out in this work suggest that an analysis of diffusional decay functions is helpful for the study of exchange in partially filled porous samples.

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