Diffusion processes in mesoporous adsorbents probed by NMR

Rustem Valiullin · Muslim Dvoyashkin

Abstract In this contribution, we review the results of our experimental studies on diffusion of guest molecules in mesoporous solids using pulsed field gradient (PFG) NMR technique. Having unique potentials to non-invasively probe the microscopic diffusion processes in pores, this method may provide quintessential information on the character of molecular propagation for different pore morphologies and fluid phase state. In particular, different modes of molecular diffusion in partially filled pores may be separately probed and the overall diffusion process could be analyzed taking account of the details of the inter-phase coexistence. In addition to the dynamic properties, some information concerning the distribution of guest molecules within the porous matrix may also be obtained.

Keywords Diffusion · Mesoporous materials · NMR · Inter-phase equilibrium · Fluid distribution

1 Introduction

Diffusion is one of the most fundamental phenomena in nature, involved in a majority of physico-chemical and biological processes. In many of them, it often plays a key role determining, e.g., the efficiency of a process or controlling its evolution in a particularly defined way. This may be exemplified by referring, e.g., to microporous catalysts, like zeolites. In such materials, substantial confinement effects lead to a dramatic decrease of the diffusivity of the guest molecules as compared to the bulk phase, often rendering the overall processes to a diffusion-limited regime (Kärger and Ruthven 1992). Similar examples may be found also in the bio-world, e.g. in cells, where the confinement-induced restrictions of molecular mobility by the cell membranes and internal compartments are involved in cell functioning. With respect to the adsorption-related sciences, molecular diffusion is an ubiquitous ingredient of all sorption processes and defines a kinetic equilibrium between the adsorbed and surrounding bulk-like phases.

Over the last few decades, much progress has been done in elucidating the structure-dynamics relations in microporous materials, having an indispensable technological importance. Current progress in adsorption- and diffusion-related sciences and in the synthesis of porous solids gave rise to a new family of hierarchical materials with the transport channels of mesoscalic dimension as an essential part of their structure (Barton et al. 1999; Schüth et al. 2002). Optimal transport properties, which may be achieved using these materials, brought them into the focus of modern technological interest. In turn, the quantification of the diffusion properties of guest molecules under mesoscopic confinement has thus become quintessential. At the same time, not only the high transport rates make these materials so attractive. It is already well established that mesoscalic ensembles often exhibit novel properties (Gelb et al. 1999). Molecular diffusivity, being a very sensitive quantity to various local interactions, may be used as an intrinsic internal probe of the physical processes occurring on mesoscales. However, to make this step, a more detailed understanding of the diffusion process in such materials is highly desirable. Although computer simulations represent a powerful tool, which may provide the required information (Monson 2005), the experimental methods, such as NMR, still play an important role. First of all, irrespective of enormous progress in computer simulations, some processes re-

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quiring big particle ensembles and long time spans are still not accessible by this technique. Therefore, the experimental methods not only provide new information on physical processes, but the results obtained may also be considered as precursors for further improving and validating of the simulation methods.

In the present contribution, we review the main points of our experimental studies of adsorbate self-diffusion processes in mesoporous matrices using the PFG NMR method. By profiting from its potentials to non-invasively probe the internal microscopic dynamics (Stallmach and Kärger 1999), we have been able to confirm and, in some cases, to find out some general patterns in diffusion behavior of guest molecules in mesopores under different conditions. To illustrate all these observations, we may confine ourselves to presenting the experimental data only for the well-known Vycor porous glass as a host material.

2 PFG NMR basics

The basics of NMR may be found in many textbooks (Callaghan 1991; Kimmich 1997; Price 1997; Stapf and Han 2005), and here we only briefly recapitulate the most essential points related to the diffusion measurement. In principle, there exist two different approaches to probe molecular transport properties. In the first of them, one creates a concentration gradient and follows it subsequent equilibration. The latter may be simply measured using NMR spectroscopy basing on the fact that the NMR signal intensity is directly proportional to the number of nuclear spins in the sample under study. Thus, increasing, e.g., the gas pressure above a porous material in the NMR sample tube one may follow the kinetics of adsorption of the molecules from the gas phase (Valiullin et al. 2006). Because the density in the gas phase is much lower than in the adsorbed phase, the measured quantity will predominantly refer to the amount adsorbed. The analysis of the thus obtained kinetic curves using a relevant model will yield the so-called transport diffusivity. This quantity consists of contributions from both self-diffusion and cooperative modes of molecular transport.

Self-diffusivity, i.e. molecular random motion under equilibrium conditions, is most elegantly measured by PFG NMR. This method is based on the application of a gradient of the magnetic field over the sample for a short period of time. In this way, a position-dependent phase encoding of the nuclear spins is achieved. After the system a certain time has been given to evolve, the same gradient pulse, but with the opposite sign, is applied. During this time, often called diffusion time, the nuclei-bearing molecules may change their initial positions due to diffusion. The purpose of the second decoding pulse is to compensate the phase acquired by the spins in the encoding period. Because of diffusion, the overall dephasing is not complete. This leads to an attenuation of the observed spin-echo signal. Such an experimental procedure may be easily treated analytically to yield the characteristics of the underlying diffusion process. Thus, under the short gradient pulse approximation (Price 1997), the measured spin-echo signal intensity S is nothing else than the Fourier transform of the "average diffusion propagator" $P(x, t_d)$ (Kärger et al. 1988), namely the probability that molecules will displace by x during time t_d:

$$S(q, t_d) = \int P(x, t_d) e^{iqx} dx. \qquad (1)$$

Here, q is the wave number which is primarily defined by the strength of the magnetic field gradient. In the simplest case of the purely random process with a Gaussian propagator with the corresponding diffusivity D, typical of most bulk fluids, the spin-echo attenuation is given by

$$S(q, t_d) = S(0, t_d) \exp\{-q^2 D t\}. \qquad (2)$$

Thus, independently controlling in the experiments q and the diffusion time t_d, one may non-invasively assess microscopic diffusion properties of the molecules in mesoporous solids.

3 Diffusivity as a function of the pore filling

Mesoscalic molecular ensembles found, e.g., in mesopores, exhibit a rich variety of phenomena upon varying the external conditions (Gelb et al. 1999). These include, in particular, shifts of the evaporation and capillary-condensation transitions with a well-pronounced hysteresis phenomenon (Everett 1967). Being intrinsically related to the different density distributions at equal external conditions, this was expected to show up as well in the patterns of molecular propagation. Indeed, our first experiments with mesoporous silicon have shown that, in parallel to adsorption hysteresis, there is also the phenomenon of "diffusion hysteresis" (Naumov et al. 2007; Valiullin et al. 2004). The diffusivities measured on the adsorption and desorption branches as a function of the external gas pressure exhibit quite a complex behavior. All these features are clearly seen in Fig. 1, where the diffusivities for cyclohexane in Vycor porous glass measured at diffusion time $t_d = 10$ ms (no dependence of the diffusivities on t_d is found on the time scale from 5 to 100 ms) are shown as a function of the external pressure (Kärger et al. 2005; Valiullin et al. 2005a). Such type of measurements can be easily done using the experimental setup shown in Fig. 2. Adsorption and desorption of the liquids is performed by use of a big reservoir connected to an NMR glass tube where the porous material is placed. The

Fig. 1 The adsorption-desorption isotherms (*circles*, *right axis*) and the effective diffusivities D_{eff} (*triangles*, *left axis*) for cyclohexane in Vycor porous glass vs. the relative pressure $z = P/P_s$ on the adsorption (*open symbols*) and the desorption (*filled symbols*) branches. (From Valiullin et al. 2005a)
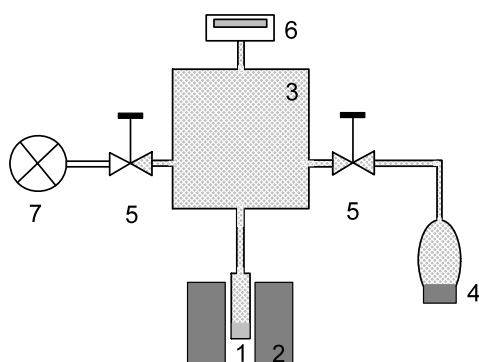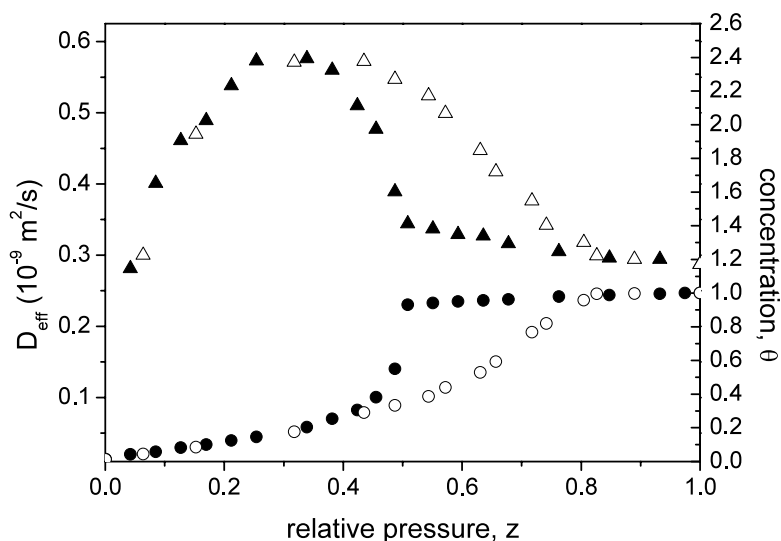
Fig. 2 Schematic of the experimental setup for diffusion measurements at different pressures: *1*—NMR tube with porous material; *2*—NMR spectrometer; *3*—buffer reservoir; *4*—flask with liquid; *5*—manual valves; *6*—pressure detector; *7*—turbo-molecular pump

volume of the reservoir exceeds that of the probe substantially. The vapor pressure of the liquids in the reservoir is regulated either through a valve connected to a tube with the liquid under study (the adsorption branch) or a valve connected to a vacuum pump (the desorption branch). The vapor pressure is registered using a digital manometer. First of all, qualitative correlations in the diffusion and adsorption data may be identified. In this respect, in what follows, we shall separately discuss three different representative regions, namely (i) a region of complete pore filling by the capillary-condensed phase, (ii) a region of only (sub-)monolayers and multilayers on the surface, and (iii) the hysteresis region where (i) and (ii) coexist with each other.

At sufficiently high pressures, all pores in the host material are completely filled by the capillary-condensed liquid. Due to a tortuous structure of Vycor porous glass (Kikkinides et al. 2000) the diffusivity in the pores is lower

than that of bulk cyclohexane ($D \approx 1.4 \times 10^{-9}$ m^2/s). Starting from the saturated vapor pressure P_s, with decreasing pressure the measured diffusivities show a well-reproducible trend to increase. In this region, the external gas pressure is still high enough to prevent triggering of the evaporation transition or cavitation within the pores. Equilibrium between the external gas phase and the intra-pore fluid is rather attained by a decrease of the density of the capillary-condensed liquid in the pores. Thus, the increase of the diffusivity with decreasing external gas pressure can be referred to the decreasing intra-pore density.
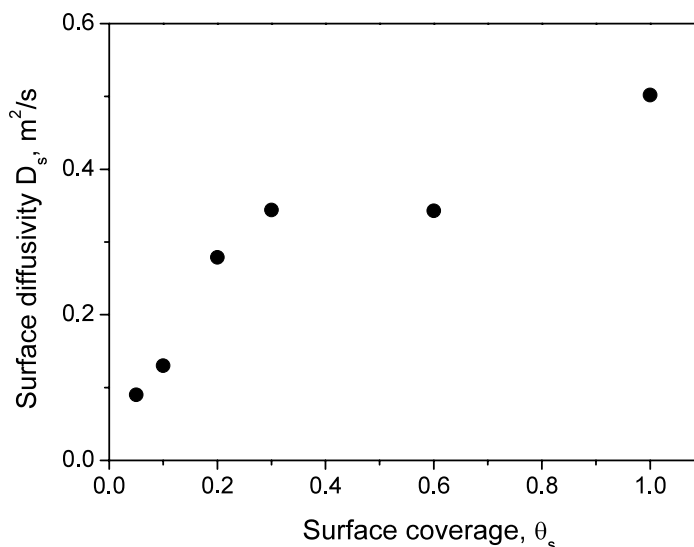
At low pressures, namely from minimal ones accessible in our setup up to the onset of the capillary condensation in the smallest pores, the gas phase in the pore interiors coexists with the molecules adsorbed on the pore walls. This gives rise to a two-mode character of the molecular propagation: surface diffusion and diffusion through the gas phase (Choi et al. 2001; Gomer 1990). During the typical observation times from milliseconds to seconds, as accessible by PFG NMR, the whole molecular trajectories within the mesopores will consist of a big number of alternating sections, corresponding to displacements along the surface and in the gas phase. Because these displacements are not correlated, they may be analyzed separately to yield the respective diffusivities (Dvoyashkin et al. 2007). Thus, the effective diffusivity D_{eff} in pores may be written as

$$D_{eff} = p_g D_g + p_s D_s, \qquad (3)$$

where D_g and D_s are the diffusivity in the gas phase and the surface diffusivity, respectively, and p_g and p_s ($p_g + p_s = 1$) are their relative weights.

Because under our experimental conditions the molecular mean-free-path is usually much longer than the mesopore

Fig. 3 Surface diffusivity of n-pentane in Vycor porous glass measured as a function of the surface coverage at 278 K

4 Surface diffusivity

One of the important modes of molecular propagation in mesoporous materials is surface diffusion (Gomer 1990). The surface area of these materials turns out to be large enough to give rise to a measurable NMR signal of the molecules adsorbed therein. In this way, surface diffusion can be measured, in particular, as a function of surface coverage. As we have seen in the preceding section, one of the complications to identify the pure surface diffusion mode may arise due to a superimposed diffusion through the gas phase. However, this may be eliminated by a proper accounting for the latter mechanism (Valiullin et al. 2005a, 2005b) or even avoided by choosing an adsorbate possessing a sufficiently low vapor pressure. Thus, by providing $p_g \ll 1$, the term $p_g D_g$ in (3) may be neglected and, consequently, the measured diffusivity D_{eff} becomes almost equal to D_s (note that $p_s \approx 1$).

Figure 3 shows the surface diffusivity of n-pentane in Vycor porous glass measured as a function of the surface coverage θ_s where the condition $p_g \ll 1$ is well hold. Importantly, the diffusivity increases with increasing θ_s, which is typical of diffusion on heterogeneous surfaces. Also, it was found that the measured diffusivities do not depend on the observation time t_d on the PFG NMR time scale from 3 to 300 ms revealing Gaussian character of the diffusion process. Diffusion on a surface may be treated as a sequence of jumps of guest molecules between neighboring surface sites, with the transition rates depending on the adsorption energy and/or possible barrier energies (Kehr et al. 2005). Due to chemical or geometrical disorder, the energies of adsorption on different surface sites may be distributed, leading to a material- and guest molecule-dependent energy landscape. Subsequently, this results in a corresponding distribution of the transition rates. At very low coverages,

dimension, diffusion in the gas phase may be considered as proceeding via the Knudsen diffusion mechanism (Pollard and Present 1948). However, owing to the adsorbed phase, the effective pore size as "perceived" by the gas phase has to be corrected for the thickness of this layer. Finally, the diffusivity in the gas phase D_g may be given as $D_g = D_K/\tau$, where D_K is the coefficient of Knudsen diffusion and τ is the tortuosity factor (Ardelean et al. 2005; Geier et al. 2002; Levitz 1993). The fraction p_g of molecules in the gas phase, can be, in first approximation, expressed as a function of the external gas pressure P as

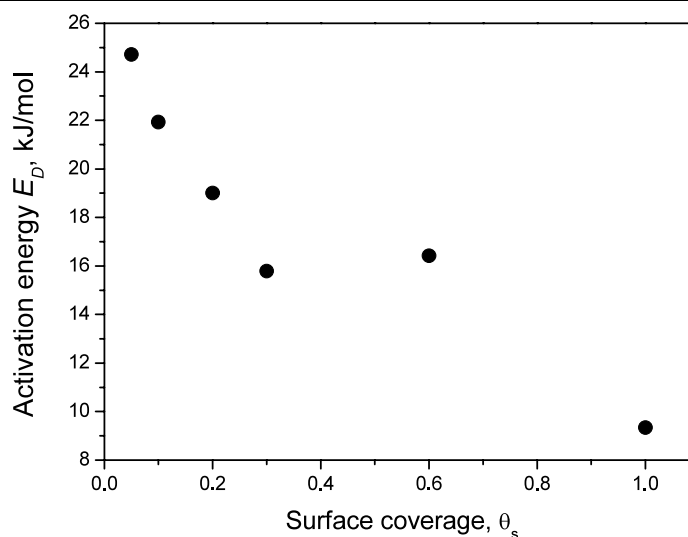$$p_g = \frac{1-\theta}{\theta} \frac{PM}{RT\rho_l}, \tag{4}$$

where θ is the normalized amount adsorbed at gas pressure P, M is the molar mass, R is the gas constant, T is the temperature, and ρ_l is the liquid density. The thus calculated term $p_g D_g$, as compared to the measured D_{eff}, is as well found to pass through a maximum and its magnitude well correlates with D_{eff} (Naumov et al. 2007). This suggests that the measured dependency of the effective diffusivity on the gas pressure P may be qualitatively understood by even these simple assumptions: At low pressures, the increase of P leads to an increase of p_g, and, consequently, to an increase of the effective diffusivity. Simultaneously, the volume accessible for the gas phase decreases, and, at a certain pressure, this mechanism takes over and leads to a decrease of D_{eff}. In general, the shape of the function $D_{eff}(P)$ depends on pore size and morphology of the porous material and the thermodynamical properties of the fluid (Ardelean et al. 2005; Courivaud et al. 2000; D'Orazio et al. 1989; Gedat et al. 2001; Valiullin et al., 2005a, 2005b, 2006). Surface diffusion is more complicated and is considered in the subsequent section.

Fig. 4 Activated energies for surface diffusion of n-pentane in Vycor porous glass as a function of the surface coverage

when the intermolecular interactions have a minor impact, the effective diffusivity is proportional to the average transition rate (Cameron and Sholl 1999). However, owing to the site-energy disorder, the latter becomes concentration dependent: with increasing surface coverage, more sites with smaller energies of adsorption are occupied. This leads to an increase of the mean jump rate with increasing θ_s (Cameron and Sholl 1999).

Additional evidence for the site-energy disorder may be provided by assessing the activation energies E_D for diffusion (Kehr et al. 2005). This quantity is easily accessed by PFG NMR by measuring the surface diffusivity as a function of temperature. We have found that in the studied temperature range the diffusivities follow the Arrhenius behavior

$$D_s = D_{s0} \exp\{-E_D/RT\} \qquad (5)$$

with E_D shown in Fig. 4 for different surface concentrations θ_s. As expected, E_D decreases with increasing surface coverage. Interestingly, at intermediate θ_s, a qualitative change in the dependency is observed. We anticipate that this is due to an increasing role of the adsorbate-adsorbate interaction at higher surface concentrations.

Adsorption measurements are often used to reveal the distribution of the surface adsorptive energies (Rudzinski and Everett 1992; Steele 1974). However, this type of measurements can hardly distinguish between different energy topologies characterized by the same site-energy distribution functions. It has been suggested (Riccardo et al. 1992) that the data on surface diffusivities may help to resolve this issue. We have shown here that PFG NMR may provide a comprehensive set of the quantitative information on molecular dynamics on the surfaces, such as the concentration dependencies of the diffusivity or the activation energy. Appropriate analytical approaches may be used to deduce from these data the required quantitative information about the surface properties.

5 Fluid distribution in random mesopores

In some materials possessing well-ordered structure, the analysis of the spin-echo attenuation functions, exhibiting characteristic diffraction-like features, may yield information about the dimension of the typical structural units of the porous medium where the diffusion takes place (Callaghan et al. 1991). Alternatively, the structural properties may also be assessed by observing patterns of the restricted diffusion measured at the low-q limit, bearing the information on different characteristics of the confining regions (Sen 2004). The same approach, under certain conditions, may also be applied to probe extension and character of the distribution of fluid regions in mesopores at partial pore fillings (Valiullin et al. 1997; Veith et al. 2004). In the latter case, one profits form the fact that the liquid-gas interface may act as a semi-permeable membrane for the molecules in the capillary-condensed phase. This results in patterns of restricted diffusion in molecular propagation at certain time scales. If this scale is within that probed by PFG NMR, the structural properties of such fluid regions may be studied experimentally.

In order to prepare a system with an inhomogeneous distribution of the fluid phase within the porous matrix, we have used a sealed NMR tube with Vycor porous glass (Dvoyashkin et al. 2007). At temperatures as low as about 230 K, only the mesopores were saturated by n-pentane. Thus it was assured that the pore filling factor is of about 1. By increasing temperature, a temperature-driven desorption from the pores can be initiated and, importantly, the pore filling factor and details of the diffusion in the pores can simultaneously be followed by NMR. At sufficiently low temperatures, corresponding to pore fillings of less than about 0.6, the spin-echo attenuations were found to follow the simple exponential form given by (2). This experimental finding

Fig. 5 The effective diffusivities for n-pentane in Vycor porous glass as a function of temperature. The *triangles* refer to the sample with precise pore filling at the lowest temperature, and the *circles* to the sample with excess liquid. (From Dvoyashkin et al. 2007)
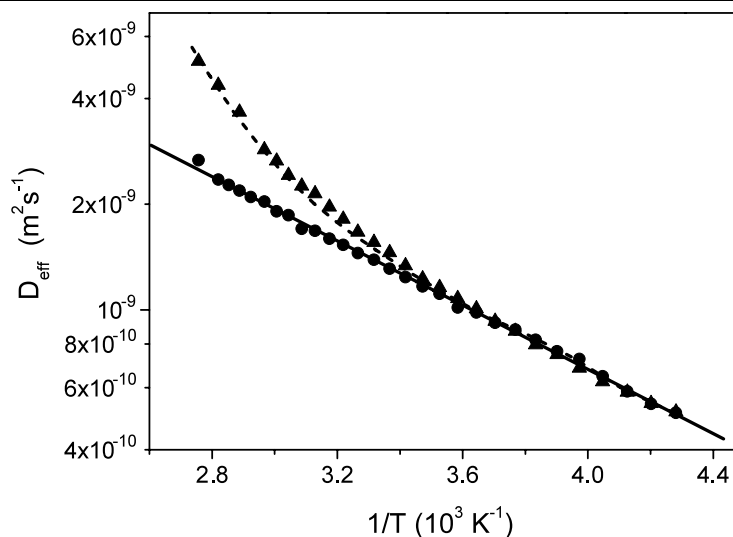
Fig. 6 Normalized spin-echo attenuations for cyclohexane in Vycor porous glass measured for different diffusion times t_d at $T = 460$ K
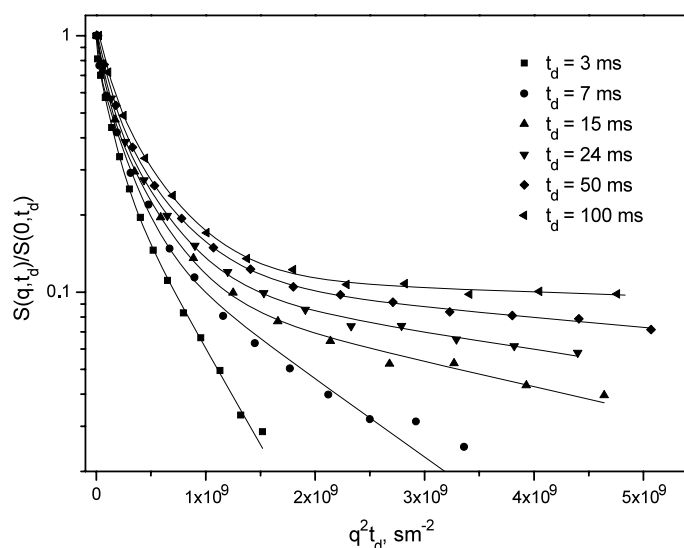
point out a homogeneous character of the diffusion process on the time scale of the experiment, i.e. all molecules may be characterized to have the same averaged dynamical properties. Figure 5 shows the diffusivities obtained by fitting (2) to the measured spin-echo attenuation functions. For comparison, the intra-pore diffusivities measured for a sample with excess liquid, i.e. not affected by an internal desorption process, are also shown. In this temperature range, the diffusion process in the latter samples follows the Arrhenius law given by (5). However, in the sample without excess liquid, temperature-driven desorption initiates a cavitation process leading to diffusivity enhancement (Dvoyashkin et al. 2007).

An even more remarkable behavior is observed upon further increase of the temperature. Here, the spin-echo attenuation functions exhibit a qualitatively novel feature. Their shape does not follow anymore that of (2), one rather observes an additional slower diffusing component. As an ex-

ample, Fig. 6 shows the spin-echo attenuations measured at 460 K for different diffusion times. Moreover, the diffusivity corresponding to this component decreases with increasing diffusion time, which is a clear indication of restricted diffusion. A formal analysis of this experimental finding (Valiullin et al. 1997) yields a value of the order of 4 micrometers for the size of the confining regions. We anticipate that these regions may be associated with regions of a continuous capillary-condensed phase formed upon fluid desorption from the pores. In this way, the character of a fluid distribution may be studied on the desorption and adsorption branches as a function of the pore filling. However, additional theoretical analysis is required to transfer the results of these experimental studies into quantitative information on microscopic structural details for such regions.

In conclusion, dynamics of guest molecules in mesoporous hosts exhibit a rich variety of phenomena strongly in-

terrelated with those defining details of the inter-phase equilibrium. NMR has unique options to simultaneously record adsorption and diffusion of the guest ensembles. The thus obtained information, further accomplished with the data on macroscopic behavior, have already shown to be a promising complementary approach to address physical process in mesopores (Valiullin et al. 2006). Further experimental studies in this direction will consolidate the basis for a profound theoretical description of the dynamics and of the details of the state of guest molecules under mesoscalic confinement.

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