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Correlating phase behaviour and diffusion in mesopores: perspectives revealed by pulsed field gradient NMR

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Porous solids represent an important class of materials widely used in different applications in the field of chemical engineering. In particular, mesoporous hosts attract special attention due to their fascinating match of transport, geometrical and chemical properties. Not only a very high specific surface area, accessible for adsorption and heterogeneous catalysis, but also their efficient transport properties are the key factors determining optimal use of these materials. Therefore, a fundamental understanding of the correlations between the phase state of confined fluids, their transport properties and the geometrical features of confinement are of particular importance. Among the different analytical techniques, nuclear magnetic resonance (NMR) is especially suited to cover various crucial aspects of the highlighted issues. In this work, we provide a short overview of recent advances related to the interrelations of phase behaviour and diffusion in mesoporous materials studied using various NMR techniques.

I. Introduction

Since the discovery of the M41S-family of molecular sieves by the researchers of Mobil Oil Corp.,1,2 a plethora of ordered mesoporous materials with different compositions and surface properties was found including, for instance, the materials of the SBA-, HMS-, MSU-, TUD-, or CMK-type,3–8 periodic mesoporous organosilicates (PMOs),9 mesocellular silica foams (MCFs)10–12 or metal–organic frameworks (MOFs).13–15 The continuing interest in these materials, especially in view of applications in sorptive separations and heterogeneous catalysis, relies, inter alia, on their high specific surface areas and their large pore diameters with respect to the conventionally applied zeolites and related microporous materials. As a consequence, sorptives and reactants with considerably larger molecular dimensions have access to the inner surface area of these molecular sieves.16

Moreover, a more rapid mass transfer into and egress of mesoporous materials offers obvious potential over their microporous counterparts.17,18 Mesopores have often been invoked to serve as “transport pores” for higher molecular reactants and, thus, enable and accelerate their transport to the active sites of solid catalysts.19 Prominent examples are the alkylation of benzene with propene to cumene over dealuminated mordenite-type zeolites20 or fluid catalytic cracking (FCC) of long-chain hydrocarbons over acidic faujasite-type zeolites.21 While in the sooner case, the mesopores are introduced into the catalyst by dealumination of the zeolite crystals, a mesoporous matrix around the zeolite crystallites provides access to the active surface sites in the latter. It was recently shown by pulsed field gradient (PFG) NMR that a transport optimization of FCC catalysts can be achieved by selecting a matrix for the active zeolite crystals.

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with the appropriate mesopore size.\textsuperscript{22} The introduction of mesopores into the acidic faujasite catalyst by steam dealumination, however, does not have a pronounced effect on the hydrocarbon diffusivities within the micropores of the zeolite.\textsuperscript{23} Besides catalysis, mesoporous materials are attractive for the adsorptive uptake of substances with larger molecules such as enzymes for biocatalysis\textsuperscript{24} or pharmaceuticals for controlled drug release.\textsuperscript{25,26} Other potential application areas for mesoporous molecular sieves include nanofluidics, photonics, and optical switches.\textsuperscript{27–29}

In addition to the apparent advantages regarding mass transfer, mesoporous materials exhibit most interesting properties with respect to the thermodynamic equilibria of the adsorbed phases. In addition to the dense “phase” adsorbed on the pore walls, there are solid, liquid, gaseous or supercritical phases within the pores with equilibrium and transition conditions significantly differing from those in the bulk\textsuperscript{30,31}. This difference is a result of the confinement of the phases within the mesopores. In contrast, micropores are, for most substances, too small for another phase but a dense adsorbed phase to exist and in macropores the influence of the walls on the phase behaviour within the pores is almost negligible. Apparently, the conditions for phase transitions are especially well-defined for ordered mesoporous materials, i.e., for materials with a narrow pore size distribution as typical for molecular sieves.

The deviation of the conditions for phase equilibria or transitions under confinement, in particular by mesopores, from those of the bulk is a general phenomenon and not limited to particular phases. For instance, both the liquid/gas and the solid/liquid coexistence curves and, consequently, the critical and the triple point are shifted towards lower temperatures and pressures compared to the bulk. Moreover, a rich set of experimental data is available to date revealing, with a sufficiently high accuracy, proportionality of these shifts to the reciprocal mesopore size. Thus, the dependence of the solid/liquid phase transition (melting point) on the mesopore diameter is routinely used nowadays for the determination of the mesopore diameter by thermoporometry.\textsuperscript{32–34} The same principle is exploited also in gas adsorption porometry.\textsuperscript{35} It is worth noting that a better understanding of these phenomena may be of indispensable practical relevance in most diverse fields, ranging from material science to biophysics.\textsuperscript{36–38}

From the known phenomenon of sorption hysteresis, however, it is evident that the phase behaviour within mesoporous materials can be rather complex and that it depends on the way it is approached.\textsuperscript{39} Although these basic features have been reported long ago,\textsuperscript{40,41} a complete understanding of the phenomenon is still lacking. Beside fundamental interest, the practical importance of the problem is determined by the fact that the measurement of gas adsorption is widely used as a classical characterization technique\textsuperscript{35} and, in turn, is of enormous importance in the development of novel porous materials.\textsuperscript{42,43}

While a wealth of studies is devoted to the nature and the thermodynamic equilibrium of phases within mesoporous solids, much less investigations were carried out to describe and understand the transport properties of mesopore-confined phases. It is obvious, of course, that the presence of different phase states or distributions will strongly affect the corresponding transport properties within the mesopores. This perspective focuses on diffusion within mesoporous materials in view of the behaviour of liquid and gas phases coexisting inside the mesopores. With respect to the theme of this special issue, the scope of this article is, thus, the treatment of the phases as “molecular assemblies”, rather than the behaviour of isolated molecular species in confined spaces of porous solids. The most important industrial applications of mesoporous materials, especially in sorption and heterogeneous catalysis, involve gas and/or liquid phases, not only in the bulk surrounding of the materials, but also within the mesopore space (vide supra). Other phase equilibria inside mesoporous solids such as those of solid/gas or solid/liquid systems will, thus, not be treated here.

Based on our previous experience, it is another goal of this article to highlight how transport measurements, especially by pulsed field gradient (PFG) NMR, can be used to infer on the phase behaviour within mesoporous solids. The information obtained from transport measurements is shown to be complementary to that typically extracted from sorption equilibrium data such as isotherms or isochores, i.e., from the loading of the sorbutes as a function of the physical properties of the fluid phase outside the porous solid.

The present article is subdivided into five major sections. First, we describe the specific phase behaviour in mesopores and its partly significant differences from that in bulk phases. As mentioned above, this contribution will be restricted to the liquid/gas-coexistence and the related phenomena near the critical point. After a brief outline of how PFG NMR can be applied to measure different transport-related properties within porous solids (for more detailed description of this method the readers may refer to ref. 44–49), two following sections will be focused towards the transport processes occurring in porous solids on the different porosity scales (micro- and macroporosity). Finally, we will summarize the current knowledge on the relation of transport properties and phase behaviour in mesoporous solids at conditions for which a transition of the pore-confined phases to the supercritical state occurs. We will give selected examples where this
transition and the presence of a supercritical phase in the mesopores were utilized for applications in materials preparation, sorption, and heterogeneous catalysis. From the current knowledge, we will derive potential perspectives as to where and how the specific liquid/gas-phase behaviour and its effects on transport properties in mesoporous materials may be utilized in the future and outline the open scientific questions and challenges.

II. Fluid phase equilibria in mesopores

It is well known that the phase coexistence of fluids in porous solids is altered as compared to the bulk fluids. This is demonstrated by the sorption isotherms, a typical example of which is shown in Fig. 1. The shape of an isotherm reflects the interactions of the adsorbed molecules with the internal surface of the porous material as well as the effect of confinement on properties of the adsorbed fluid. At sufficiently low external gas pressures \( P \) the latter unequivocally determines the equilibrium between molecular ensembles adsorbed on the pore walls and the surrounding gas phase. This means that the sorption process, i.e., adding or releasing of molecules to or from the adsorbed (multi-)layers, is continued until the chemical potential equilibrates over the whole system. Notably, there are no imposed barriers of either type to prevent the equilibration under these conditions. At intermediate pressures, a sudden change of the amount adsorbed is observed, which is attributed to evaporation or capillary-condensation transitions. Importantly, both transitions occur at pressures well below the saturated vapour pressure \( P_s \), manifesting the confinement effect upon the phase state. In addition, an important feature of mesoporous materials is the occurrence of hysteresis, where for a range of bulk gas pressures the sequence of states encountered on desorption does not coincide with that encountered on adsorption.

The pioneering theories of adsorption and hysteresis in pores are usually classified as capillary condensation theories. They are typically constructed around the idea of a shifted capillary condensation and evaporation transitions due to curved menisci, i.e., by considering equilibrium between the condensed phase with a curved meniscus in the pores and its vapour just above it. As a result, this situation may often be described by the famous Kelvin equation for the transition pressure \( P_{tr} \),

\[
\ln \left( \frac{P_{tr}}{P} \right) = \frac{1}{\Delta \mu} + \frac{1}{\Delta \mu_0} \quad \text{where} \quad \Delta \mu_0 = \Delta \mu - \frac{4 \sigma}{r},
\]

where \( \sigma \) is the surface tension and \( r \) is the pore radius. Morphologically, the presence of a supercritical phase in the system persists in a local minimum of free energy. This is argued, for example, that narrow interconnections between large pores could delay the evaporation of liquids from them. This is the so-called pore-blocking effect, which was later widely used to describe the hysteresis phenomenon in random porous materials.

Later on, density functional theories (DFT) and lattice gas models capturing microscopic features of the adsorption phenomena have been developed. Applying DFT to uniform pores, with increasing external vapour pressure the molecular ensemble in pores is found to remain in a gas-like state beyond the point of the true thermodynamical transition, i.e., the system persists at a local minimum of free energy. The same is true for the desorption process concerning a liquid-like state. Importantly, microscopic theories thus point out the metastable character of the transitions. To extend these theories to real porous materials, i.e., to allow the simultaneous coexistence of gas-like regions and regions with a capillary-condensed phase, one has to artificially incorporate effects of the geometrical heterogeneity of pore structure.

A more detailed analysis of realistic molecular ensembles under confinement using statistical thermodynamics has become possible due to the rapid progress of computer technologies. Exploiting quite different approaches, many details of phase equilibria in various model systems have been elucidated and rationalized.

In particular, the results obtained using non-local DFT pointed out that in sufficiently big pores condensation occurs at the vapour-like spinodal, while desorption takes place at the equilibrium. The same conclusion has been drawn using molecular dynamics simulations of the molecular behaviour in one- and both-ends open pores. Moreover, this approach allowed the authors to address also the phenomenon of pore blocking, which is widely accepted to contribute to the development of hysteresis. Thus, using an ink-bottle pore as confining geometry, it was found that liquid can evaporate from a large cavity even if the neck of the ink bottle remains filled with the capillary-condensed phase. On the other hand, other studies confirmed the relevance of the pore-blocking mechanism.
emphasizing the importance of the details of the pore structure and the involved interactions.

Progress in fabrication of nanoporous materials with well-defined structural properties made it possible to validate all these theoretical predictions by experimental means. Thus, using ordered mesoporous silica materials composed of spherical cage-like pores connected with each other by cylindrical pores and using different adsorptives, different regimes of desorption, namely controlled by pore-blocking or cavitation, have been identified.\(^{65,66}\) In particular, cavitation-controlled evaporation in ink-bottle pores with the neck size smaller than a certain critical value has become evident. In pores with larger necks, evaporation was found to be percolation-controlled. Remarkably, the results obtained with seemingly simpler pore geometry revealed less consistency with the theoretical expectations. Thus, on the basis of recent experimental studies using MCM-41 silica material with well-defined open-ended cylindrical pores, it was concluded that capillary condensation rather than evaporation takes place near a normal one of the bulk, but typically reveals a pore size-dependent temperature shift of the upper closure point.\(^{85-87}\)

For the confined fluids, this point at the temperature \(T_{ch}\), called hysteresis critical point and corresponding to vanishing hysteresis, had earlier been considered as a counterpart of its bulk value \(T_c\). This, however, has to be treated with caution. Indeed, in addition to the hysteresis critical temperature, one may as well define the pore critical point at \(T_{cp}\).\(^{54}\) The latter is defined as the temperature where a jump in the adsorption isotherm just disappears. In particular, cavitation events over a certain pressure range. The obtained results unequivocally pointed out that \(T_{ch} < T_{cp} < T_c\)\(^{88}\). A simple explanation of the obtained relation \(T_{ch} < T_{cp}\) could be provided by recalling the metastable character of the condensation and evaporation transitions in the hysteresis regime. With increasing temperature, the local free energy minima may become sufficiently small to be bypassed by the thermal fluctuations.\(^{50}\) Thus, the hysteresis loops would collapse at lower temperatures compared to \(T_{cp}\).

III. Pulsed field gradient NMR

Nuclear magnetic resonance provides direct access to the key data of fluid behaviour in the porous space of interest: it is able to simultaneously record the number of molecules and their dynamical properties. Thus, measuring the NMR signal intensity in a sample of a porous solid as a function of the external gas pressure, one may compile the respective adsorption isotherm, as an indicator of the phase state in the pores. On the other hand, a number of other quantities may simultaneously be measured in the same sample under the same conditions. One of them, which will be in the focus of this review, is molecular translational mobility. Therefore, NMR may serve as a self-consistent experimental tool allowing to correlate phase state of a fluid in pores and its transport properties. The way in which this becomes possible may be
rationalized using the classical interpretation of nuclear magnetism.44,46,89

Under the influence of a magnetic field of intensity \( B_0 \), each nucleus (i.e., the nuclear \( \text{“spin”} \)) performs a precessional motion about the direction of \( B_0 \) with the angular frequency \( \omega_0 = \gamma B_0 \), where \( \gamma \) is the nuclear gyromagnetic ratio. By the application of a radio-frequency field of the same frequency \( \omega_0 \) over a well-defined short interval of time, the net magnetization in the sample can be turned from the direction of the magnetic field (the equilibrium position) into the plane perpendicular to it. The net magnetization rotating in this plane induces a voltage in the receiver coil surrounding the sample under consideration. The thus measured voltage is monitored as the NMR signal. Obviously, the intensity of this signal is proportional to the number of respective nuclei and hence to the number of molecules in the sample (one should, however, take account of nuclear magnetic relaxation effects, which for fluids in pores may be significant and may lead to relaxation weighting of the measured signal). The different Larmor frequencies of different nuclei (e.g., \(^1\text{H}, ^{13}\text{C} \) or \(^2\text{H}\)) provide an additional option to separately track different species.

For rationalizing the way in which the translational mobility of the fluid molecules may be quantified, we consider the influence of field inhomogeneities on the Larmor frequencies \( \omega_0 \) of the nuclear spin system under study. Applying a magnetic field linearly increasing in the \( z \) direction, \( B = B_0 + \gamma g z \), \( \omega_0 = \gamma B_0 + \gamma g z \) becomes a function of the \( z \) coordinate. With this inhomogeneous field held for a time \( \delta \), each spin will acquire a phase \( \phi = \gamma B_0 \delta + \gamma g \delta \int_0^\delta z(t) \, dt \). This procedure is sometime called “position-dependent phase encoding”. In the basic version of pulsed field gradient (PFG) NMR the sample is subjected to two pulses of “field gradients” of constant amplitude \( g \) and of duration \( \delta \) with separation \( t_d \). With two such pulses of opposite gradient directions, to the end of the second pulse re-phasing may not be complete and the phase difference \( \Delta \phi \) is given by:

\[
\Delta \phi = \gamma g \left( \int_0^\delta z(t) \, dt - \int_{t_d}^{t_d+\delta} z(t) \, dt \right). \tag{3.1}
\]

It now becomes obvious that, being able to detect \( \Delta \phi \), one immediately gets access to the difference of the locations of the individual molecules at the instants of the gradient pulses. Here, we imply that the short-gradient approximation, namely \( \delta \ll t_d \), is fulfilled and thus we may neglect the effects of molecular motion during the gradient pulse.45–47 This is especially justified under our experimental conditions performed with the use of ultra-high gradient strength.90 Implementing these field gradient pulses into an appropriate sequence of radio-frequency pulses, e.g., Hahn91 or stimulated-echo92 pulse sequences, one is able to determine the resulting NMR signal, the so-called spin echo. It may be shown that the attenuation \( S(q, t_d) \) (from now on we use the widely used notation \( q = \gamma g \delta \)) of this signal intensity,91

\[
S(q, t_d) = \int P(z, t_d) e^{i q z} \, dz, \tag{3.2}
\]

is nothing else than the Fourier transform of the so-called mean propagator \( P(z, t_d) \), one of the key functions describing the internal dynamics in complex systems.93 \( P(z, t_d) \) denotes the probability density that, during time \( t_d \), an arbitrarily selected molecule is shifted over a distance \( z \) in the direction of the applied field gradient. The range of molecular displacements observable by PFG NMR spans over a few orders of magnitude from about 100 nm, accessible by means of strong field gradients,94 to a few mm. On the PFG NMR time scale from about 1 ms to 1 s, the former displacements can be observed in high molecular mass polymeric systems95 or for strongly confined fluids,96 while the latter displacements are typical for gas phase applications.97 As an important point in comparison with other spectroscopic techniques, NMR has to operate with relatively big molecular ensembles of about \( 10^{18} \). Being a disadvantage, to require the presence of such a huge ensemble of molecules, on the other hand, well-averaged quantities are provided.

For unrestricted, normal diffusion, the propagator results as the solution of Fick’s second law with the initial concentration given by Dirac’s \( \delta \)-function:

\[
P(z, t) = \frac{1}{\sqrt{4\pi D t}} \exp \left\{ -\frac{z^2}{4 D t} \right\}, \tag{3.3}
\]

with \( D \) denoting the self-diffusivity. Inserting eqn (3.3) into (3.2) yields a spin-echo diffusion attenuation of exponential form:

\[
S(q, t_d) = \exp(-q^2 D t_d). \tag{3.4}
\]

Thus, the diffusivity (and the mean square displacement, respectively) may be easily determined from the slope of the semi-logarithmic representation of the intensity of the NMR signal versus the squared pulse gradient “intensity” \( \delta g \). Note, that for the sake of simplicity, \( S(q, t_d) \) in eqn (3.4) is given as normalized to \( S(0, t_d) \) to account for nuclear relaxation effects. Often, as a useful approximation, eqn (3.4) may be assumed to hold when molecular propagation deviates from normal, unrestricted diffusion. In such cases, the quantity \( D \) has to be interpreted as an “effective” diffusivity defined by Einstein’s equation \( D = \langle z^2(t) \rangle / 2 t \) (which, clearly, coincides with the real diffusivity as soon as the prerequisites of normal diffusion are fulfilled). For anomalous diffusion \( D \) is not a constant and depends on the observation time.98,99

Deviations of \( S(q, t_d) \) from the exponential shape of eqn (3.4) may also result from a distribution of molecular mobilities along the sample. An important example, in the context of the present review, is a sample composed of a powder of small porous particles. For such materials, two molecular ensembles characterized by different diffusivities may easily be distinguished, namely those in the inner pore space and those between the porous particles. Very generally, the spin-echo diffusion attenuation for such two-phase systems (here, by “phase” we refer to transport characteristics of the diffusing species rather than to the physical state) may be written as:95,100

\[
S(q, t_d) = \int \Psi(t_a, t_b) \exp\left\{ -q^2 \left( D_a t_a + D_b t_b \right) \right\} \, d\Omega. \tag{3.5}
\]

Here, \( \Psi(t_a, t_b) \) is the joint probability density that, during the observation time \( t_d = t_a + t_b \), a molecule spent the times \( t_a \) and \( t_b \) in the phases a and b, respectively. \( \Omega \) denotes a certain
pair \( \{\tau_a, \tau_b\} \). A particular solution of this problem under the assumption of an exponential lifetime distribution in the phases may be found in ref. 101.

It is instructive to consider two limiting cases of slow and fast molecular exchange between the phases. In the first case, all individual molecular trajectories are confined to either of the phases, i.e. there exist only two possible time pairs \( \Omega_1 = \{\tau_a = \tau_{a,b}, \tau_b = 0\} \) and \( \Omega_2 = \{\tau_a = 0, \tau_b = \tau_d\} \). The relative fractions of such trajectories, or corresponding values of \( \Psi(\tau_a, \tau_b) \), ultimately coincide with the fractions \( p_a \) and \( p_b \) (\( p_a + p_b = 1 \)) of molecules in the two phases a and b, respectively. Therefore, the respective diffusion attenuation function is given by the sum of two exponents:

\[
S(q,t_d) = p_a \exp(-q^2D_a t_d) + p_b \exp(-q^2D_b t_d). \tag{3.6}
\]

Another limit of fast exchange corresponds to situations when all molecules during \( t_d \) experience many consecutive travels in both phases, i.e., if the molecular lifetimes in both phases are much shorter than the total diffusion time \( t_d \). In this case, assuming that the ergodic hypothesis is fulfilled, namely \( \tau_a(\tau_{a,b}) = \tau_{a,b} \), we may substitute \( \tau_a \) and \( \tau_b \) in eqn (3.5) by \( p_a t_d \) and \( p_b t_d \) respectively. Hence, \( \Psi(\tau_a, \tau_b) = 1 \) when \( \tau_a = p_a t_d \) and \( \tau_b = p_b t_d \) and zero otherwise. Finally, in this limit eqn (3.5) becomes:

\[
S(q,t_d) = \exp(-q^2D_a t_d) + \exp(-q^2D_b t_d). \tag{3.7}
\]

In between these two regimes, \( S(q,t_d) \) can be described by eqn (3.5) with a continuous spectrum of the apparent diffusivities \( (\tau_a D_a + \tau_b D_b) t_d \), where \( \tau_a \) varies from 0 to \( t_d \). By performing inverse Laplace transform one may, in principle, access the function \( \Psi(\tau_a, \tau_b) \) containing all information about the exchange process between the two phases. This, however, is an ill-posed problem, which only recently is becoming of practical use by extending the experiments to the second dimension. 102–104 More practically, by performing the experiments with different observation times \( t_d \) one can, with a relatively high accuracy, measure the fraction \( p_d \) of molecules which have not left a phase with the slowest diffusivity \( D_d \) during \( t_d \). Obviously, \( p_d(t_d = 0) \) is the relative fraction of molecules in this phase. The measured \( p_d(t_d) \) can be related to the molecular lifetime distribution function \( \psi(\tau) \) in the corresponding phase \( \text{via:}^{95}

\[
\frac{p_d(t_d)}{p_d(t_d = 0)} = 1 - \int_0^{t_d} \psi(\tau) \, d\tau. \tag{3.8}
\]

In section VB, this relation will be shown to provide the basis for the so-called NMR tracer desorption technique. Alternatively, due to the short time scale of PFG NMR in comparison with “conventional” tracer exchange experiments, this method is as well referred to as “fast tracer desorption”. 96,105–107 The function \( \psi(\tau) \) is a key function of the internal dynamics of stationary populations quite in general, and of particular relevance for catalytic processes involving porous solids. In ref. 108, 109, as part of a “network of characteristic function”, it is shown to directly yield such (further) important functions like the tracer exchange curve and the effectiveness factor of a chemical reaction between compounds of equal diffusivities.

The function \( \psi(\tau) \) describes, in particular, how fast a molecular ensemble, initially residing in a particle, exchanges its molecules with the surrounding. Thus, for a spherical particle of radius \( R \) and an intra-particle diffusivity \( D \), for diffusion-limited exchange (i.e., with no surface barriers, hindering the molecules to leave the particle at the interface with the surrounding phase) \( \psi(\tau) \) is given by ref. 110

\[
\psi(\tau) = \frac{6D}{R^2} \sum_{m=1}^{\infty} \exp\left\{-\frac{m^2 \pi^2 D \tau}{R^2}\right\}. \tag{3.9}
\]

Note that the case of surface barriers may also be analyzed in this way. 111 With a known function \( \psi(\tau) \) one may easily estimate the average time \( t_d \), after which the molecules leave the particle in which they just reside. For spherical particles, it immediately follows from eqn (3.9) that:

\[
t_{av} = \int_0^\infty \tau \psi(\tau) d\tau = \frac{R^2}{15D}. \tag{3.10}
\]

On the other hand, by tracking the fraction of molecules which did not leave the porous particles during the experimental observation time \( t_d \), one may estimate an average size of the particles. To do this, one may fit eqn (3.8) with \( \psi(\tau) \) given by eqn (3.9) to the experimental data. In this case, the only fitting parameter is \( R \) while the diffusivity is known in advance from the analysis of the respective spin-echo diffusion attenuations.

To conclude this section, in recent years NMR progressed to provide a wealth of approaches to analyze different aspects of molecular dynamics in porous materials with inhomogeneities in the porous structure on very different length scales, 112–114 including its possibility to quantify molecular diffusivities in mesopores under different external conditions. The simultaneously measured NMR signal intensity provides the option to correlate the transport properties with the phase state in the pores. Moreover, by stepwise changing the external conditions, e.g., the vapour pressure, one may create a gradient of the chemical potential between the gas phase and the confined fluid allowing to follow its equilibration by means of NMR. In this way, the results of macroscopic and microscopic techniques may be compared to reveal information on the fluid behaviour, which so far, was inaccessible. 115,116 Altogether, a set of NMR approaches allow to address various aspects of molecular dynamics in mesoporous adsorbents of different pore architecture and macro-organization.

**IV. Microscopic diffusivity in monoliths**

In what follows, we are going to address different aspects of molecular dynamics in mesoporous materials. Referring, e.g., to heterogeneous catalysis involving porous catalysts, the whole molecular trajectories consist of diffusion paths within the porous particles intermitted by those in the free space between the particles (see Fig. 2). We will proceed by first considering the transport mechanisms within mesopores. Depending on various conditions, primarily those determined by the phase state of a fluid, these include surface diffusion, diffusion of molecules in multilayers, Knudsen diffusion and diffusion in the capillary-condensed phase. In disordered materials, e.g., random porous glasses, different molecular
phases may coexist with each other in vastly different configurations, yielding, in their combination, very complex behaviours. The latter is evident even from a quick review of the literature data on diffusion in mesopores, reporting a wide spectrum of behaviour depending on pore size, adsorbate and surface properties, temperature, etc. refs. 117–124. Let us now start by considering some of these transport modes separately.

A Surface diffusion

Among the different mechanisms of molecular transport, surface diffusion plays a significant role, sometime being the dominating mechanism of the mass transfer through porous solids. Quite generally, it may be associated with a thermally-activated hopping motion of the guest molecules along the surfaces (see, e.g., the reviews125–127). For experimental studies of surface diffusion, two different approaches are commonly used. One of them is based on the creation of a gradient of the chemical potential (e.g. via pressure or concentration gradients) and measuring the resulting fluxes. In this way, the so-called coefficient of transport diffusion is measured. It contains information about both single-molecule and cooperative modes of the molecular transport. Another approach is designed to operate under equilibrium conditions by, e.g., “labelling” a molecule and following its trajectory.128–131

Such direct visualizations of the molecular trajectories on surfaces have illuminated many novel phenomena, like molecular clustering or mobility enhancement due to a specific molecule-substrate interaction. The analysis of the thus obtained single trajectories yields the so-called tracer diffusivity. Notably, exactly this quantity is as well probed by PFG NMR. The huge surface area of mesoporous adsorbents makes NMR applicable to probe surface diffusivity at sub-monolayer surface coverage.122 Importantly, this latter technique provides an ensemble-averaged quantity.

The required surface coverage \(c\) (also referred to here as concentration) may conveniently be prepared by tuning the external gas pressure in contact with the mesoporous material. Such a setup can easily be implemented to the \textit{in situ} operation in an NMR spectrometer,124 so that the adsorption (free induction decay (FID) signal intensity which is proportional to the number of spins in the sample) and diffusion (PFG NMR) could simultaneously be probed. Fig. 3 illustrates this possibility by showing the diffusivity of acetone in mesoporous silicon. The material was prepared by electrochemical etching of a (100)-oriented silicon wafer with a resistivity of 10 \(\Omega\) cm using a current density of 30 mA cm\(^{-2}\) in an electrolyte containing 50% aqueous solution of HF and \(\text{C}_2\text{H}_5\text{OH}\) in a volume ratio of 2 : 1. In this way, a foam-like structure with an average pore diameter of about 4 nm is formed.133 First, the adsorption isotherm has been compiled by measuring the FID signal intensity \(S\) as a function of the gas pressure. By using the BET equation,134 the amount adsorbed corresponding to one monolayer surface coverage was estimated and used for transformation to the surface concentrations \(c\). The surface diffusivities \(D_s\) measured in parallel, are, thereafter, plotted \textit{via} \(c\). Note that the originally obtained diffusivity data have been corrected (although the correction was minor) for the diffusion through the gaseous phase in the pore interior. This procedure will be explained in more detail in the following section.

The most important message of Fig. 3 is that the diffusivity increases with increasing surface coverage. This is in contrast to what one expects for hard-core particles on homogeneous surfaces, where an increase of the number of particles leads to a decrease of the space available for diffusion. Due to this so-called site-blocking effect the surface diffusivity would rather decrease with increasing \(c\). Remarkably, heterogeneity of the surface, \textit{e.g.}, site or saddle-energy disorder, inverts this trend. In a most simple way, this may be understood by considering the effect of site-energy disorder given by a distribution \(f(E)\) of site energies \(E\). Due to the activated character of the jump process, this leads to a corresponding distribution of the jump rates, with the latter being \(W(E) \propto \exp[-E/RT]\).

With such a condition, the solution of the diffusion problem for a single particle is obtained in the frame of the so-called random trap model, resulting in a diffusivity \(D = (1/W)^{-1}\). Here, the brackets denote averaging over all surface sites and \(a\) is the inter-site distance.135,136 It is worth noting that the solution does exist only, if there exists a finite average residence time \((1/W)\) and if the model implies that there is no correlation between neighbour site energies, \textit{i.e.}, if a random energy dispersion exists.
topography is assumed. The particle ensembles may be treated similarly. However, the probabilities of site occupancy, \( p(E) \), have to be properly accounted for:

\[
D_s = \int \frac{f_s(E)p(E)W^{-1}(E)}{E} dE. \tag{4.11}
\]

Forbidding multiple site occupancies, \( p(E) \) has naturally to be chosen to follow the Fermi–Dirac statistics, \( p(E) = (1 + \exp((E - \mu)/RT))^{-1} \), where \( \mu \) is the chemical potential of the surface ensemble. Such an occupancy factor explains increasing diffusivity with increasing surface coverage or, correspondingly, chemical potential: A new particle added to the system will occupy a site with a lower surface energy as compared to those already occupied. Therefore, the overall transition rate, obtained by averaging over the whole ensemble, will increase.

To illustrate the basic predictions of eqn (4.11), it is more convenient to use it in a modified form:\(^{137,138}\)

\[
D_s = D_0 \frac{(1 - c)^2}{c} \exp \left( \frac{\mu - E_{av}}{RT} \right), \tag{4.12}
\]

where \( E_{av} \) is the average site energy and \( D_0 \) is the diffusivity of a single particle on the surface with the only site energies \( E_{av} \).

Owing to the equilibrium conditions, the chemical potential of the surface ensemble is equilibrated with that of the external gas phase. In the first order, the latter may be approximated by the ideal gas, i.e., \( \mu = \mu_0 + RT \ln(z) \), where \( z \equiv P/P_0 \). Thus, by absorbing all concentration-independent parameters into \( D_{0*} \), eqn (4.12) becomes

\[
D_s = D_0^* \frac{(1 - c)^2}{c} z. \tag{4.13}
\]

This equation shows the direct interrelation between the surface diffusivity \( D_s \) and the adsorption isotherm \( c(z) \) (or, vice versa, \( z(c) \)). Let us now consider one of the typical isotherms used for the analysis of adsorption on heterogeneous surfaces, for example the generalized Freundlich isotherm:\(^{139}\)

\[
c = \left( \frac{Kz}{1 + Kz} \right)^m. \tag{4.14}
\]

In eqn (4.14) \( K \) is a constant and \( 0 < m < 1 \) is a parameter reflecting the degree of surface heterogeneity. The meaning of the parameter \( m \) may intuitively be understood by comparing eqn (4.14) to the Langmuir isotherm given by the same equation but with \( m = 1 \). The latter is valid for homogeneous surfaces, i.e. the addition of a new particle to the surface depends only on surface coverage. If, however, \( m < 1 \), the affinity of the surface decreases with increasing coverage, reflecting, thus, its heterogeneity. With an isotherm as given by eqn (4.14), the surface diffusivity will behave as demonstrated in Fig. 4 for different values of \( m \). As expected, the diffusivity increases with increasing surface coverage. However, at intermediate coverage, \( D_s \) passes through a maximum. The latter is the result of two competing mechanisms-entropic (site-blocking) and energetic (increasing transition rates) ones.

Let us now analyze the experimental data shown in Fig. 3 in this way. The inset shows the low-pressure part of the adsorption isotherm for acetone in porous silicon. It may be fitted using eqn (4.14) with \( m = 0.26 \). Remarkably, the diffusivity data at low surface coverage nicely follow the pattern \( D_s^*e^{-1/m-1} \) (low-c limit of eqn (4.13)), with \( m = 0.26 \) obtained from the isotherm. Note that this functional dependence is expected to hold for \( c < 0.2 \), while in our case the range is extended up to \( c \approx 0.8 \). However, we consider this to occur accidentally. More detailed understanding and description of the surface diffusivities at intermediate and high coverage requires a proper account of, e.g., particle distribution over the surfaces.

In this subsection we did consider transport along the surfaces only. If, however, the molecules possess sufficient kinetic energy to overcome the energetic barrier to get away from the surface, they may perform movements along the gas phase in the pore interior. Before discussing the combined effects of different transport modes, we would like to address some aspects of pure diffusion in the gaseous phase under confinement.

**B Diffusion in the gas phase**

The coefficient of gas diffusion \( D_{gas} \) in random pore networks is generally represented as the diffusivity in a well-defined reference system (denoted in what follows by the subscript 0), divided by a tortuosity factor \( \tau \).\(^{140,141}\) For the two extreme cases, namely dominating molecule-molecule collisions (bulk diffusion, subscript b) and dominating molecule-wall collisions (Knudsen diffusion, subscript K), one thus may note

\[
D_K = \frac{D_{0K}}{\tau_K}, \quad D_b = \frac{D_{0b}}{\tau_b}. \tag{4.15}
\]

As a reference system for Knudsen diffusion one generally considers an infinitely long pore with a diameter equal to the mean intercept length \( d \) of the real pore space, yielding:\(^{142}\)

\[
D_K = \frac{1}{4\pi d^2} \tag{4.16}
\]
with \( \bar{u} = (8RT/\pi M)^{1/2} \) as the mean thermal speed and \( R, M \) and \( T \) denoting, respectively, the gas constant, molar mass and absolute temperature. For gas diffusion one has:

\[
D_g = \frac{1}{6} \lambda. \tag{4.17}
\]

with \( \lambda \) as the molecular mean free path. In the general case, by considering the overall diffusion resistance as the sum of the diffusion resistance by molecule-molecule and molecule-wall interaction, one has\(^{143}\)

\[
\frac{1}{D_{\text{gas}}} = \frac{1}{D_k} + \frac{1}{D_b}. \tag{4.18}
\]

The limiting cases of Knudsen and of bulk diffusion as described by eqn (4.16) and (4.17) easily result from this relation by considering the respective inequalities \( \lambda \gg d \) and \( \lambda \ll d \). The mean free path in the gas phase is generally notably larger than the mesopore dimensions. Therefore, diffusion in mesopores is generally subjected to Knudsen diffusion. Obviously, partial pore filling decreases the effective pore diameter, resulting in the relation\(^{122,124}\)

\[
D_k = \frac{d}{3} \sqrt{\frac{8RT(1-\theta)}{\pi M}}. \tag{4.19}
\]

Gas diffusion in the space of macropores, such as the inter-crystalline space in beds of nanoporous particles, may occur to cover the whole range between the limiting cases of Knudsen diffusion and bulk diffusion. Thus, under conditions where the intraparticle diffusion becomes negligibly small for overall mass transfer, the effective-diffusivity conception (see next section) allows a straightforward measurement of gas phase diffusion by PFG NMR. With an appropriately chosen loading, PFG NMR self-diffusion measurement with sealed samples (isochoric conditions) allows, by a corresponding temperature variation, to cover the regimes of both dominating Knudsen diffusion (low temperatures) and bulk diffusion (high temperatures).\(^{144-146}\)

Most importantly, in this way for the first time direct experimental evidence was provided\(^{141}\) that, on following the conception provided by eqn (4.15) to (4.18), the limiting cases of bulk diffusion and Knudsen diffusion have to be described by notably different tortuosity factors. In particular, in the Knudsen regime molecular propagation is found to be impeded by tortuosity effects much more intensely than under the conditions of bulk diffusion. Following refs. 147–149, this finding may be referred to an enhanced anti-correlation of subsequent molecular displacements during Knudsen diffusion in random pore networks. This means that during Knudsen diffusion-in addition to the same tortuosity-related enhancement of the diffusion path lengths as during bulk diffusion-there is an enhanced probability of backward-directed molecular displacements after collision with the pore wall. The findings of the PFG NMR diffusion measurements were nicely reproduced in mesoscopic kinetic Monte Carlo simulations with beds of zeolite NaX.\(^{150}\)

Anti-correlation of molecular displacements after wall encounters is expected to intensify with increasing wall roughness. Both kinetic Monte Carlo simulations\(^{151-156}\) and analytical considerations\(^{151}\) confirm this assumption. Moreover, the kinetic Monte Carlo simulations\(^{154-156}\) revealed coinciding effects on the transport diffusivity and on the self-diffusivity, i.e. on the molecular propagation rates under both non-equilibrium and equilibrium conditions.\(^{157,158}\) Since, quite generally, for non-interacting diffusing particles transport diffusion and self-diffusion have to coincide and since during Knudsen diffusion, by its very nature, any interaction of the diffusants is excluded, this is exactly the behaviour to be expected.

### C The effective diffusivity

With the two mechanisms of molecular transport in mesopores discussed, the overall one may be defined by both of them weighted appropriately. Before we will correlate these weights with the details of the phase equilibrium, let us consider two limiting situations: (i) at relatively low vapour pressures, before the onset of capillary condensation and (ii) at higher pressures, when the capillary-condensed bridges (small domains of the liquid extended over the whole pore cross-section) are formed. In the former case (i), the molecular displacements in both of the phases, the liquid one adsorbed on the pore walls and in the gaseous one in the pore interior, may proceed in parallel to each other. Thus, the problem becomes similar to that of a parallel connection of the resistivities. Therefore, the solution for the effective diffusivity \( D_{\text{eff}} \) is given by ref. 159 and 160

\[
D_{\text{eff}} = p_{\text{gas}}D_{\text{gas}} + p_{\text{liq}}D_{\text{liq}}. \tag{4.20}
\]

where \( D_{\text{gas}} \) and \( D_{\text{liq}} \) are the diffusivities in two phases and \( p_{\text{gas}} \) and \( p_{\text{liq}} \) are the respective weights \( (p_{\text{gas}} + p_{\text{liq}} = 1) \). Note that the first term (in particular at sufficiently high temperatures) may notably exceed the second one. It is due to this reason that the effective diffusivity of liquids adsorbed in beds of porous materials may be significantly larger than in the real liquids. As to our knowledge, such a situation has been discovered for the first time in ref. 161 and has been reproduced in numerous subsequent publications, e.g., ref. 71,144 and 162.

In contrast, in the latter situation (ii) the propagation through a medium composed of two regions may require alternation between two regions. In the limiting case this is similar to the problem of sequential connection of resistivities. A corresponding general solution for the effective diffusivity \( D_{\text{eff}} \) is ref. 160

\[
\frac{L_{\text{gas}} + L_{\text{liq}}}{D_{\text{eff,s}}} = \frac{L_{\text{gas}}}{p_{\text{gas}}D_{\text{gas}}} + \frac{L_{\text{liq}}}{p_{\text{liq}}D_{\text{liq}}}. \tag{4.21}
\]

where \( L_{\text{gas}} \) and \( L_{\text{liq}} \) are the typical extensions of the regions occupied by the gas and liquid volumes, respectively, and \( p_{\text{gas}} \) and \( p_{\text{liq}} \) are the respective densities.

The phase state is reflected by the adsorption isotherm \( \theta(z) \), where \( \theta \) is the amount adsorbed (also referred to as the pore filling factor) at the relative pressure \( z = P/P_s \) (with \( P_s \) denoting the saturation pressure). One may start to relate \( p_{\text{gas}} \) and \( p_{\text{liq}} \) to the given phase state with the set of equations:

\[
N_{\text{gas}} + N_{\text{liq}} = N, \tag{4.22}
\]

\[
V_{\text{gas}} + V_{\text{liq}} = V. \tag{4.23}
\]
where \( N_{\text{gas}} \) and \( N_{\text{liq}} \) are the number of molecules in the gaseous and liquid phases and \( V_{\text{gas}} \) and \( V_{\text{liq}} \) are the volumes occupied by them. The latter may be expressed as \( V_i = mN_i/\rho_i \), where \( \rho_i \) is the density in a phase \( i \), and \( m \) is the molecular mass. With \( \theta = V_{\text{liq}}/V \) and taking account of \( \rho_{\text{liq}} \gg \rho_{\text{gas}} \) it immediately follows that

\[
\rho_{\text{gas}} = \frac{1 - \theta \rho_{\text{gas}}}{\theta} \rho_{\text{liq}}, \tag{4.24}
\]

The density \( \rho_{\text{gas}} \) may be related to the external gas pressure \( P \) via the ideal gas law

\[
\rho_{\text{gas}} = \frac{zPM}{RT}, \tag{4.25}
\]

where \( M \) is the molar mass. Thus, the effective diffusivity appears to be correlated with the isotherm, similarly to eqn (4.13) obtained for the surface diffusion.

It is clear that eqn (4.20) well holds for mesoporous materials with relatively big pore sizes and in the regimes where there are mono- and/or multi-layered molecules on the pore walls. To demonstrate the behaviour of \( D_{\text{eff}} \) under these conditions, we have prepared mesoporous silicon samples with an average pore diameter of 10 nm. The recipe for their fabrication was similar to that given in section IVA, with the only differences in the doping level of the silicon wafer (resistivity of 10 m\( \Omega \) cm) and the anodization current density (80 mA cm\(^2\)). The acetone diffusivities measured in this material are shown in Fig. 5 as a function of the amount adsorbed \( \theta \). To do this, first the diffusivities had been measured as a function of the gas pressure and, using the simultaneously measured adsorption isotherm (not shown), the diffusivities were re-plotted versus \( \theta \). It is important to note that the isotherm reveals the onset of capillary-condensation being located at \( z \approx 0.7 \), corresponding to \( \theta \approx 0.6 \). Thus, up to \( \theta \approx 0.6 \), the multi-layered molecules on the pore walls coexist with the gaseous phase in the pore interior (parallel configuration), so that the use of eqn (4.20) is justified.

One immediate consequence of eqn (4.24) is that \( \rho_{\text{gas}} \) passes a maximum upon variation of \( \theta \). This is due to two competing effects, namely the increase of the gas density (controlled by \( z \)) and the decrease of the relative fraction of molecules in the gaseous phase (given by \( (1 - \theta)/\theta \) with increasing \( P \). Indeed, at low pore loadings (\( \theta \leq 0.2 \)), because of the adsorbate-surface interaction, the external pressure \( P \) must be appreciably decreased in order to release molecules from the surface. Thus, the term \( z \) in eqn (4.24) determines the behaviour of \( \rho_{\text{gas}} \) at low loadings. With increasing \( \theta \), the situation is reversed, and the contribution of the gaseous phase to overall diffusion becomes dominating. Finally, however, with \( \theta \to 1 \) and thus \( \rho_{\text{gas}} \to 0 \) (eqn (4.24)), the gas phase contribution vanishes. Hence, irrespective of the fact that, with \( \theta \to 0 \), the term \( (1 - \theta)/\theta \) goes to infinity, \( \rho_{\text{gas}} \) faster approaches zero, so that \( \rho_{\text{gas}} \) becomes negligibly small.

Let us quantify these statements. As shown by the dotted line in Fig. 5, at intermediate loadings (\( \theta \) from about 0.2 to 0.6) the magnitude of the term \( \rho_{\text{gas}}D_{\text{gas}} \) in eqn (4.20), where \( D_{\text{gas}} \) is given by eqn (4.19), is calculated to be comparable to the diffusivity at full saturation. With the adsorbed phase, the situation is less obvious, since we do not have an equivalent model for molecular diffusion in multi-layers. As a first approximation, however, we assume that the diffusivity does not appreciably change with the pore loading and that it is equal to the diffusivity at full pore loading. At sub-monolayer coverage the diffusivity behaves as shown in Fig. 3. Thus, the calculated overall dependence of the diffusivity in the adsorbed (liquid) phase on pore loading \( (\rho_{\text{gas}}D_K + (1 - \rho_{\text{gas}})D_c) \) results as that shown by the solid line in Fig. 5. It appears that it satisfactorily describes the experimental finding, except for a small difference in the region of the multi-layer adsorption. This reflects an underestimation of the diffusivity within the layer. With only these data, however, we do not yet feel ourselves totally confident that the diffusivity of the multi-layered molecules exceeds that of the capillary-condensed molecules, though they would clearly support such a conclusion.

The situation changes upon forming regions filled by the capillary-condensed liquid since, thus, the gaseous phase domains become spatially isolated (combination of parallel and sequential connections). Under such conditions, according to eqn (4.21), the overall diffusivity is predominantly controlled by the phase with the slowest diffusion. A nice exemplification of such a behaviour is provided by the diffusion behaviour in MAST activated carbon sample (MAST Carbon Ltd., Guildford, U.K.). Its structure is schematically shown in the inset of Fig. 6. The material used in this work was composed of 1 mm-big particles with a highly-networked internal pore structure. In addition to the micropores, there are incorporated isolated spherical holes with diameters of about 30 nm. The pore volumes of the micro- and mesopores are roughly identical.

Fig. 6 shows the diffusivity of cyclohexane in this sample as a function of the external gas pressure \( P \). In the figure the latter is presented by the gas density \( \rho_{\text{gas}} \) calculated via eqn (4.25). The diffusivity increases with increasing gas pressure up to about \( \rho_{\text{gas}} = 0.25 \text{ kg m}^{-3} \). This region corresponds to the mesopores filled by the gaseous phase. Further increase of \( \rho_{\text{gas}} \) is accompanied by the onset of capillary condensation in the mesopores, which nicely correlates with the deviation of the measured diffusivities from the
with different transport properties, one may clearly distinguish between two molecular ensembles surrounding gas phase under equilibrium conditions. Here, example—a mesoporous monolith in contact with the surroundings.

We start our consideration with the probably most simple situation. It may be thought as a model sample—i.e., a mesoporous silicon chip composed of small chips with different thicknesses. Different symbols refer to different diffusion times td from 5 to 300 ms. First of all, we note a multi-exponential dependence as expected via eqn (4.20) for dominating gas phase diffusion (dotted line in Fig. 6). Now, due to a specific arrangement of the volumes occupied by the two phases, the transport should be described by a combination of eqn (4.20) and (4.21), namely by the appropriately weighted sum of these two equations rather than by eqn (4.20) alone. A correspondingly designed dependency is shown by the solid line and yields satisfactory agreement with the experimental data.

V. Macroscopic transport

Typically, the majority of porous materials are available as powders, i.e., they are composed of solid particles with an internal pore structure. Moreover, the pore structure itself may have different levels of organization, i.e., different types of porosities and length-scales. Thus, the overall molecular transport ultimately involves molecular exchange between regions with different mobilities. The state of the fluid and, hence, its transport properties in these various regions depend in a complex way on the external conditions. The objective of this section is to demonstrate how the NMR technique may be used to address such problems. Among different examples, a particularly interesting one will be to demonstrate how NMR allows a self-consistent comparative analysis of the data on molecular transport provided by macroscopic and microscopic measurements.

A Molecular exchange between porous monoliths and their surroundings

We start our consideration with the probably most simple example—a mesoporous monolith in contact with the surrounding gas phase under equilibrium conditions. Here, one may clearly distinguish between two molecular ensembles with different transport properties, viz. molecules within the mesopores and in the surrounding phase. Thus, as discussed in section III, by recording their diffusivities one is able to attribute the molecules to either of these ensembles, and, moreover, one may monitor the exchange process between these two ensembles. Exchange times become directly accessible if they are within the time-scale of PFG NMR (1–10⁴ ms).

Under such circumstances, the most efficient method to quantify the exchange process is to follow the time-dependent fraction of molecules having the diffusivity D_{eff}.

We illustrate this approach by considering a model sample with pre-defined structural characteristics. The experimental results may thus be easily compared with the theoretical predictions. The sample consists of mesoporous silicon chips prepared by electro-chemical etching of silicon crystals. The parameters of the etching procedure and the initial silicon porosities were chosen to yield pores with a diameter of about 6 nm. After formation of a thin porous layer, they were removed from the substrate. Thus, the thus formed pores have immediate contact to the surroundings at both ends of the layer, rendering essentially one-dimensional uptake and release processes. Five different films with different thicknesses L of 10, 20, 29, 41 and 52 µm were prepared and mixed with the respective masses m = 29, 45, 50, 40 and 15 mg. The thus composed sample, consisting of porous films of different thicknesses, was, thereafter, outgassed in a NMR glass tube and brought into contact with a vapour of cyclohexane at 60 mbar. After equilibration the tube was sealed.

Fig. 7 demonstrates the normalized spin-echo diffusion attenuations for this model sample obtained using the 13-interval pulse sequence at different observation times t_d from 5 to 300 ms. First of all, we note a multi-exponential...
Eqn (5.26), calculated with all relevant parameters known, is shown in Fig. 8. It is found to nicely reproduce the experimental data. In addition, the perfect agreement suggests that the molecules may leave the initial particles without any imposed restrictions, in contrast to situations often encountered with microporous adsorbents.

In reality, the distribution of particle sizes is often not known. In this respect, it is instructive to analyze the short-time behavior \( p_d(t_d) \). Applying Poisson’s summation formula to eqn (5.27) one may show that in this limit \( p_d(t_d) \) is given by:

\[
\lim_{t_d \to 0} p_d(t_d) = 1 - 4D_{sl} t_d \left( \frac{1}{L} \right). \tag{5.28}
\]

The inset in Fig. 8 shows the fit of eqn (5.28) to the data at short times, yielding an effective average particle size of about 23 μm. This is again in excellent agreement with the expected value of 22 μm. The result of this subsection demonstrates that the described method may be satisfactorily applied to study the molecular exchange between macroparticles and the surrounding phase in the case of smooth particle exchange at the interface. Moreover, if the exchange is notably influenced by additional transport resistances at the interface between the crystal and the surroundings, significant deviations from the dynamics predicted by eqn (5.28) occur. These deviations may, in turn, be used for a quantification of surface barriers, as to be shown in the next section.

**B Surface barriers**

Most techniques for studying mass transfer in porous media are based on following the rate of molecular uptake or release by the individual particles. They are referred to as macroscopic or mesoscopic techniques of observation,\(^{168-170}\) depending on whether the whole bed of nanoporous particles or an individual particle is in the focus of observation. A model-free discrimination between internal and external transport resistances, i.e., an unambiguous separation between the influences of intraparticle diffusion and of surface barriers, however, necessitates the measurement over path lengths notably below the particle sizes which is provided by the microscopic techniques only.

As explained in the preceding section, PFG NMR is able to determine the relative amount of molecules \((p_d(t_d)/p_d(0))\) in eqn (3.8) and (5.26)), which have not yet left the particles which they accommodated at time \( t_d = 0 \). Under the conditions of gas phase adsorption, the signal of the gas phase is negligibly small so that in this case \( p_d(0) = 1 \) and there is no need for normalization by dividing \( p_d(t_d) \) by \( p_d(0) \). For variable \( t_d \), this information is exactly that of a tracer exchange curve \( \gamma(t_d) \), with \( \gamma(t_d) = 1 - \frac{p_d(t_d)}{p_d(0)} \) denoting the relative amount of (labelled) molecules which, after time \( t_d \), have left a particular porous particle, being replaced by other (unlabelled) ones from the surroundings and/or other particles. This special ability of PFG NMR is exploited by the so-called NMR tracer desorption technique, to which we have referred to already in section III.

The experimentally accessible tracer exchange curve \( \gamma(t_d) \) may most conveniently be correlated with the governing
transport mechanisms via the method of moments.\textsuperscript{96,171,172} Thus, e.g., the “first” moment
\[ f_0^t (1 - \gamma(t)) dt \equiv f_0^t p_{av}(t)/p_{av}(0) dt = f_0^t \psi(t) dt = t_{av} \] (5.29)
is easily identified as the molecular mean life time within a particular porous particle (which, in eqn (3.10), has been referred to as \( t_{av} \)), and where, in addition, we have made use of eqn (3.8). Most importantly, different transport resistances simply appear in the first moment as a sum of the terms corresponding to each individual resistance on its own.\textsuperscript{96,171,172} Thus, assuming spherical particles, with eqn (3.10) for diffusion-limited exchange and with the corresponding expression for exchange processes governed by the surface permeability (\( t_{av,barr} = R/3z \)), the general case may be noted as
\[ t_{av} = t_{av,diff} + t_{av,barr} = \frac{R^2}{15D} + \frac{R}{3z}, \] (5.30)
where the surface permeability \( \chi \textsuperscript{96,173} \) is defined as the ratio between the flux through the particle surface and the difference between the actual boundary concentration of the diffusing species under study and the concentration, which eventually, would be established in equilibrium with the surrounding atmosphere.

Thus, with the value of \( D \) directly determined by PFG NMR with sufficiently short observation times (diffusion path length during observation time much shorter than the particle size), the value of \( t_{av} \) following via eqn (5.29) from the “NMR tracer desorption curve” and the particle radius \( R \) accessible by microscopic inspection, the surface permeability follows directly from eqn (5.30). This option has been widely exploited for the exploration of the conditions under which either the production of zeolitic host systems\textsuperscript{174,175} or their technological applications can be performed with single crystallites with dimensions (favourably a few nanometres). These channels are hexagonally arranged in an internal porosity of about 40\%. As a next level of organization, the crystallites form clusters or grains with a dimension of a few hundred nanometres. Finally, the grains agglomerate to particles with a broad distribution of sizes from tens to hundreds of micrometers.

The diffusion attenuation functions for cyclohexane measured in the sample under study have been found to be slightly non-exponential and to depend on the observation time \( t_d \) which was varied from 3 to 300 ms. Such a behaviour is an indication of a macroscopic heterogeneity with the time-dependence being the consequence of the molecular exchange between different regions in the sample. In what follows, we are going to analyze the effective diffusivities \( D_{eff} \) deduced from the attenuations in the low-\( q \) limit. The thus obtained values of \( D_{eff} \) represent the ensemble-average over the sample and are shown in Fig. 10 as a function of the external gas pressure. With a value of \( 10^{-7} \) m\(^2\)/s using the Einstein relation \( \langle \chi^2 \rangle = 6D_{eff}t_d \), the extension of the regions with a uniform diffusivity may be estimated to be \( \sqrt{6D_{eff}t_d} \approx 40 \mu \text{m} \). The latter appears to be of the order of the particle sizes. Therefore, the heterogeneity may be associated with the textural differences in the different particles.

To understand the pressure dependence of the diffusivity one may perform an analysis similar to that given in section IVC.
In this case, also equilibrium between the mesopores in crystallites and the macropores formed between the grains and the particles has to be taken into account. In this way, one finally gets

$$D_{\text{eff}} = \frac{\rho_{\text{gas}} \lambda \bar{v}}{\rho_{\text{liq}} \eta \theta} \left( a + (1-a) \frac{d_g}{d_g + \lambda} \right), \tag{5.31}$$

where $\lambda$ and $\bar{v}$ denote the mean free path and mean molecular velocity in the gas phase, $\eta$ is the ratio of the meso- and macropore volumes, $d_g$ is the effective inter-grain distance, and $a$ is the ratio of the intra-particle macropore volume to the total macropore volume, respectively. The best fit of eqn (5.31) to the experimental data is attained with $a = 0.16$ and $d_g = 0.61 \mu m$ (all other parameters are known) and is shown in Fig. 10.

A more detailed analysis of eqn (5.31) suggests that the obtained dependency of $D_{\text{eff}}$ on the gas pressure is predominantly controlled by the equilibrium conditions between the gaseous and adsorbed phases in the mesopores. Thus, the slight decrease of $D_{\text{eff}}$ observed for decreasing pressures from $z = 1$ till the onset of the evaporation transition in mesopores may be referred to the decrease in the gas density $\rho_{\text{gas}}$ in the macropores. At $z \approx 0.3$, the evaporation of the liquid out of the mesopores leads to a sudden increase of the relative fraction of the molecules in the macropores. In the low-pressure region the equilibrium is determined by the interaction of the liquid with the walls of the mesopore. Thus, the equilibrium conditions reasonably well explain the obtained results. Quantitative agreement between theory and experiment is clearly obtained only, if the characteristic geometrical features of macroporous space are taken into account. These are predominantly reflected by the diffusivity of the gas phase in the macropores. In the present case, it has been simply accounted for by summing up the transport resistivities due to intermolecular collisions and collisions with the grain walls.

Being able to record the rate of molecular displacements over different length scales, PFG NMR is able to assess the limiting processes of mass transfer in agglomerated catalyst particles formed by nanoporous crystals dispersed in a (macroporous) binder. As a prominent example, in Fluid Catalytic Cracking (FCC) catalyst particles with radii $R_p$ of typically about 30 $\mu m$ are applied which contain small zeolite crystals of type NaY with radii $R_c$ of about 0.5 $\mu m$. In such materials it is not obvious whether overall exchange with the surrounding atmosphere is controlled by mass transfer through the binder or by mass exchange between each individual zeolite crystal and the surrounding binder. In fact, following an old tradition in overestimating the transport resistance of the genuine zeolite pore network, reactant and product transport within the zeolites is generally considered to be the rate-limiting process of overall mass transfer. However, recent detailed PFG NMR studies revealed exactly the opposite. In fact, by choosing the observation time $t_d$ of the PFG NMR experiment in such a way that the experimentally covered molecular displacements are either much larger or much smaller than the zeolite crystallites, one is able to directly measure the diffusivities for molecular transport both within the individual zeolite crystals ($D_c$) and through the whole catalyst particle ($D_p$). With these diffusivities and the corresponding radii, eqn (3.10) allows a straightforward estimate of the respective time constants of molecular exchange. As a result, molecular mean life times within the individual zeolite crystals turned out to be much smaller than the mean life times within the catalyst particles, indicating that molecular transport through the particle rather than through the zeolitic component is the rate-controlling process in the overall mass transfer. During technical application, inter-crystalline exchange may clearly become impeded by the formation of surface resistance. In this case, replacing eqn (3.10) by eqn (5.30), one also has to take account of surface resistance (i.e., a finite value of the surface permeability $\gamma$).

VI. Phase state and transport

A Dynamics in disordered pores under sub-critical conditions

So far, we have clearly demonstrated that the diffusion behaviour of guest molecules in mesoporous solids is strongly coupled to their phase state in the pores. The latter can be associated with a certain point on the sorption isotherm. As a very essential property of these materials, however, one has to be aware of the development of hysteresis. Thus, under identical external conditions, the phase state becomes dependent on the way how these conditions have been attained, i.e., on the “history”. It, thus, becomes quite interesting to compare the intrinsic diffusivities in the hysteresis region.

This type of experiments can be easily carried out by performing PFG NMR diffusion measurements using NMR samples with a porous material connected to a reservoir with the vapour of a liquid under study. Thus, either by decreasing or increasing the vapour pressure in the reservoir, the effective diffusivities can be measured along with the sorption isotherm. Fig. 11 shows one of the typical examples, demonstrating a well-pronounced hysteresis loop when the diffusivity is plotted versus the external gas pressure. It should be noted that such an approach has earlier been used.
to demonstrate that nuclear magnetic relaxation properties of adsorbed fluids may also differ for adsorption and desorption.\textsuperscript{189} We could show that this type of diffusion hysteresis is not limited to systems exhibiting adsorption hysteresis,\textsuperscript{190} but also holds for other types of hysteretic behaviour, for example freezing/melting hysteresis.\textsuperscript{191}

Recalling the discussion of section IVC, the development of hysteresis in diffusivity-pressure coordinates might appear to be natural. Indeed, the external gas pressure defines the amount adsorbed \( \theta \), which is, in turn, different on adsorption and desorption as given by the sorption isotherms. Thus, one may simply attribute the difference in the diffusivities \( D_{\text{eff}} \) to the difference in \( \theta \). \( D_{\text{eff}} \) may clearly also be plotted directly as a function of the pore loading \( \theta \). Remarkably, upon such a transformation, hysteresis is still preserved as shown in Fig. 12.\textsuperscript{74} Moreover, for one and the same loading, the diffusivities are also found to differ for the various “scanning isotherms”,\textsuperscript{39} i.e., for isotherm branches which result from incomplete cycles of adsorption and desorption. The thus obtained diffusivities lie in between the two main loops and it becomes obvious that, by a corresponding “tuning” of the history of pressure variation, in this way one may obtain a whole “spectrum” of arbitrary diffusivities.

As to the most important feature of the results in Fig. 12 we refer to the existence of several different diffusivities at one and the same pore loading \( \theta \). In ref. 74, two mechanisms which may contribute to the observed behaviour, have been discussed. The first one refers to the fact that, on desorption, the liquid in the regions with the capillary-condensed phase occupies a notably larger part of the pore space during desorption than during adsorption. The second mechanism is related to the differences in the microscopic distribution of the liquid phase within the porous solid.\textsuperscript{192–194} In our case, the PFG NMR data indicate that, on the micrometer length scale, such a distribution is homogeneous. The origin of different distributions on adsorption and desorption is, thus, attributed to an interplay between cavitation and pore-blocking effects, leading to the formation of more extended mesoscale regions of the capillary-condensed and gaseous phase during adsorption.\textsuperscript{74}

The multiplicity of the diffusivities in Fig. 12 may thus be related to differences in the (history-dependent) density distribution over the pore space. This conception is in good agreement with the idea of a dynamically prohibited equilibration in random systems.\textsuperscript{82,83} Notably, being separated by large barriers in the system’s free energy, these out-of-equilibrium states, associated with different fluid distributions, are found to remain stable over very long intervals of time. Quite importantly, the non-invasive and non-perturbative access to the intrinsic molecular diffusivities in the pores using PFG NMR technique allows to provide further experimental evidence of such a scenario.

In this respect, it is interesting to note that while there is a great deal of experimental data for adsorption isotherms including hysteresis, much less attention has been given to the dynamics of systems exhibiting sorption hysteresis. Notably, there were a few experimental reports indicating that equilibration kinetics may slow down in the hysteresis region.\textsuperscript{195–198} An analytical description of the observed behaviour was undertaken by involving \textit{a priori} assumptions on diffusion-controlled sorption. Thus, all features of the experiments, in particular a slowing down of uptake in the hysteresis region, have been attributed to a corresponding change of the diffusivity.

To address this issue in more detail, a comparative study of sorption kinetics and genuine diffusivities in one and the same material under almost the same external conditions have recently been performed using NMR.\textsuperscript{115,116} The experimental procedure included a small stepwise change of the external gas pressure. Thereafter, the resulting density relaxation, \textit{i.e.}, sorption kinetics, has been followed. After giving a sufficiently long time for the equilibration, the effective diffusivity \( D_{\text{eff}} \) has been measured using PFG NMR. With the thus determined value of \( D_{\text{eff}} \) and the geometry of the used mesoporous material (rod-shaped Vycor porous glass), the sorption kinetics under the condition of diffusion control can be easily predicted. Thus, with \( \theta_{0} \) and \( \theta_{\infty} \) as the amounts adsorbed
where treated in the frame of random-field Ising systems. Critical binary mixtures in porous media and successfully is reminiscent of a very slow process of phase separation of slow relaxation due to the thermally activated process of the system equilibration is governed by extremely further experimental schemes, e.g. by varying the temperature and keeping the system volume constant. This experimental procedure is easily achieved by using sealed NMR samples containing a porous material and some volume available for the vapour above it. The impact of the external parameters on the molecular diffusivities under these conditions may most illustratively be demonstrated by a comparative study of two different samples. In one of them, in the whole temperature range probed in the experiments, the liquid under study should always completely cover the porous particles. That means that the mesopores will always be filled by the capillary-condensed phase. This sample will provide a reference diffusivity of the liquid in pores as a function of temperature. The second sample has to be prepared in such a way that only at the lowest temperature the mesopores are completely filled by the liquid. Thus, by changing the temperature, one may affect the equilibrium between the vapor phase above the porous material and the adsorbed phase.

The results of such comparative experiments are shown in Fig. 14. The figure displays the diffusivities of \( n \)-pentane in Vycor porous glass as a function of temperature. The second sample has to be prepared in such a way that only at the lowest temperature the mesopores are completely filled by the liquid. Thus, by changing the temperature, one may affect the equilibrium between the vapor phase above the porous material and the adsorbed phase.

In the other sample, however, starting from about 300 K, the diffusivities deviate from those in the reference sample. Let us consider what could be the impact of the temperature on the phase state within the mesopores. Recall, first, that this sample contains an amount of guest molecules ensuring complete filling of the mesopores only at the lowest temperature. Therefore, with increasing temperature, there is a competing process between either maintaining the vapour pressure in the gas phase surrounding the porous particles saturated or maintaining the liquid phase in the mesopores intact. At lower temperatures, up to about 300 K, under saturation \( (P/P_s) \) is found to be relatively small. This is provided by the evaporation of the liquid from the pores. At temperatures above 300 K, however, the latter process cannot compensate any more the strong decrease of the relative pressure \( P/P_s \) due to the dramatically increasing value of \( P_s \). Thus, \( P/P_s \) becomes sufficient to trigger cavitation in the sufficiently large pores of the Vycor glass.

The enhancement of molecular propagation in the sample containing no excess liquid, thus, originates from the contribution of fast molecular diffusion in such cavitated regions.
of the porous structure. Molecular transport therein is considered to follow Knudsen diffusion, the simplest model one would imply under the given conditions. Exactly such a change of the phase state of the liquid in the pores, resulting in the formation of internal gas-filled regions with the establishment of extremely fast diffusion paths therein, leads to the increase in the slope of the Arrhenius plot of the diffusivity seen in Fig. 14.

C Dynamics in pores near the critical point

1 Transition to the supercritical state. At elevated pressures a transition to the supercritical state can occur. Due to their tunable properties between those of typical liquids and gases, supercritical fluids (SCFs) have widely been explored, e.g., as innovative media for chemical conversions. In particular, the gas-like diffusivities of SCFs represent an attractive advantage for heterogeneously catalyzed reactions. In fact, an accelerated mass transfer from reactants to or of products away from the catalyst surface have been invoked in numerous cases to rationalize the rate increase upon a transition from the (bulk) liquid (or biphasic) to a single supercritical reaction phase. Unfortunately, however, a clear correlation of mass transfer properties to phase behaviour, especially within the pores of nanoporous catalysts, has not been attempted so far (see also the examples from heterogeneous catalysis given in section VIC2). So far, only indirect experimental evidence on transport properties within mesoporous solids at higher pressures is provided as obtained, for instance, from the fluid densities within the pores measured by in situ FT-IR spectroscopy. In the following, the first results of a direct measurement of diffusion properties during a phase transition from the liquid into the supercritical state in mesoporous materials are summarized. These results provide a quantitative basis for the rational design of processes utilizing SCFs for extraction, sorption or heterogeneous catalysis with mesoporous solids.

For two controlled pore glasses (CPGs) with different mean pore diameters in the mesoporous range (d = 6 or 15 nm), the diffusivities in the bulk and within mesopore space were measure by PFG NMR. Starting from a liquid phase around and inside the porous materials, the diffusivities for both pore glasses follow the Arrhenius dependence on increasing temperature. At a distinct temperature below the bulk critical temperature, however, upon a small temperature increase the diffusivities in both materials increase significantly. As an example, Fig. 15b shows such a diffusivity jump for a Vycor porous glass with d_p = 6 nm. This jump in diffusivity is an indication of a phase transition from the liquid to a supercritical fluid within the pores of the material. The occurrence of the liquid/supercritical-phase transition is corroborated by the fact that the meniscus of the liquid phase above the pore glasses in the NMR tube rises strongly when reaching this temperature, as one may see in Fig. 15a. Upon reaching supercritical conditions, the density of the pore-confined phase decreases rapidly. A corresponding part of the liquid is, thus, expelled from the pores, eventually leading to the rising liquid meniscus.

Expectedly, the increase of the diffusivities in the CPGs is related to their pore diameter: the jump is more pronounced and its temperature, i.e., T_c, is closer to that of the bulk critical temperature T_c for the material with the larger pores. The diffusivity change can, thus, be directly assigned to the shift of the phase transition caused by confinement of the phases in the mesopores. Notably, the temperature shift ΔT = T_c − T_cp is linearly correlated to the reciprocal pore diameter as earlier mentioned in other studies. Above the pore critical point, the diffusivity on the mesopores of the CPGs remains essentially constant at the value given by the mean free path in the mesopore according to the Knudsen diffusion limit. Evidently, we find this value to be higher for the material with the larger mean mesopore diameter.

It is worth mentioning that the experimental diffusivity data in Fig. 15 can be quantitatively described by a simple analytical model based on gas-kinetic arguments. Here, the effective diffusivities in the pores are calculated by a weighted superposition of the diffusivities in the adsorbed phase (assumed to have a liquid density) and in the fluid phase in the interior of the pore space. The full lines in Fig. 15 denote the results of these calculations. Obviously, the experimentally observed data are well described by this simple model.

2 Selected application cases

Materials preparation. While a supercritical phase itself is an attractive medium to produce nanomaterials, in the mesopores of a solid host it may be used to introduce guests into the pores or to chemically modify the walls within the pores of a mesoporous material. Due to the high diffusivity in the supercritical state, these processes can be achieved in significantly shorter times and with a better controllable loading than with conventional liquids. If the bulk phase surrounding the solid is
also in the supercritical state, the virtually negligible surface tension of supercritical fluids may lead to a further acceleration. Two examples will illustrate these advantages.

Holmes et al.\textsuperscript{208} have demonstrated that nanostructured metals and semi-conductors within ordered mesoporous materials may be prepared with the aid of supercritical fluids. For instance, nanowires of Silicon or Germanium can be generated within MCM-41-type molecular sieves by a controlled decomposition of metal organic precursors in supercritical $n$-hexane. As opposed to conventional gas-phase procedures such as chemical vapour deposition (CVD), a complete filling of the internal pore volume can be achieved. Moreover, the metal deposition is completed within 15–30 min, whereas durations up to days are needed for the same deposition efficiency in liquid solvents. The resulting silicon-containing composite materials show a UV-photoluminescence with an emission maximum depending on the pore diameter of the mesoporous host. They are, thus, attractive as sensors or for other optical applications.

The reactive deposition of metals from supercritical fluid solutions (Supercritical Fluid Deposition, SFD) is particularly attractive for the preparation of solid catalysts.\textsuperscript{209} For this procedure, a metal organic complex is dissolved, for instance, in supercritical carbon dioxide in the presence of a solid support material. Through addition of hydrogen to the supercritical complex solution, the metal is directly deposited onto the support. Thus, both the solubilizing power of supercritical fluids (Supercritical Fluid Deposition, SFD) is particularly attractive for the preparation of solid catalysts.\textsuperscript{209} For this procedure, a metal organic complex is dissolved, for instance, in supercritical carbon dioxide in the presence of a solid support material. Through addition of hydrogen to the supercritical complex solution, the metal is directly deposited onto the support. Thus, both the solubilizing power of supercritical fluids for high-boiling compounds and the miscibility with gases like hydrogen are utilized in this application. First results for the deposition of platinum by reduction of the precursor complex cyclooctadienyl(dimethylplatinum(ii)) in supercritical carbon dioxide indicate that the SFD can be achieved in mesoporous materials such as MCM-41 ($d = 2.3$ nm), but not in microporous zeolites like silicalite-1 or beta.\textsuperscript{210}

**Sorption.** Similar to the application for materials preparation described above, the sorption of functional compounds into mesoporous materials may benefit from the presence of a supercritical pore phase. Only very few investigations on the adsorption of substances from supercritical solutions onto mesoporous molecular sieves are reported in the literature so far. However, an application of sorption on a large-pore zeolite-type molecular sieve VPI-5 from supercritical solution may serve as an example. This molecular sieve was loaded within a short time with benzoic acid, salicylic and acetyl salicylic acid.\textsuperscript{211} The resulting composite materials are of potential interest for the controlled release of pharmaceutically active compounds.

**Heterogeneous catalysis.** The ample opportunities arising from the application of SCFs in heterogeneous catalysis were already referred to above.\textsuperscript{203} It should be emphasized here again that several studies in the literature invoke the improved transfer from a bulk supercritical phase to the catalysts surface or within the pores of a catalyst for the rationalization of high reaction rates under SCF conditions. So far, however, higher diffusivities in mesoporous materials achieved by “pressure-tuning” of the bulk phase have been measured indirectly only, e.g., by inference from density measurements via vibrational spectroscopy.\textsuperscript{204} Another, most interesting way to experimentally determine the effective diffusivity is from catalytic conversions under conditions for which the diffusion inside the mesopores of a catalyst is the rate-limiting step. Such a study was systematically conducted by Arunajatesan et al.\textsuperscript{212} for the double-bond isomerization of 1-hexene over a commercially available catalyst consisting of 0.6 wt% Pt on mesoporous $\gamma$-Al$_2$O$_3$ (average pore diameter $d = 5$ nm) close to critical point of the reactant ($T_c = 231$ °C, $P_c = 31.7$ bar). Varying the reaction temperature and pressure over a wide range of conditions, the effective diffusivities were calculated as a function of reduced density applying the Thiele concept to the mesopore diffusion-limited conversion rates at steady state.

Remarkably, the effective diffusivity in the mesopores of the 0.6 Pt/$\gamma$-Al$_2$O$_3$-catalyst can be tuned close to the critical point by two orders of magnitude. This range of diffusivities is clearly broader than that observed in by PFG NMR over the CPG with a similar pore diameter (vide supra). Note, however, that the corresponding experiments were not performed for systematically varied density, but just by heating a pure liquid hydrocarbon in the presence of the mesoporous solid enclosed in an NMR tube. Most interestingly and in perfect agreement with the findings from PFG NMR measurements on the CPGs, the maximum diffusivity in the mesoporous catalyst is observed for a reduced density slightly below that of the bulk phase. This, again, indicates that particularly high diffusivities can be achieved when the pore-confined phases reach the supercritical state. It is quite challenging to see whether this transport optimization via control of the phases inside the pore space can also be fruitfully exploited for other heterogeneously catalyzed conversions over (especially ordered) mesoporous materials.

### VII. Conclusions and perspectives

Pulsed field gradient NMR has been established as a powerful tool to explore mass transfer in porous media. It allows the direct monitoring of the various constituents of overall mass transfer and the quantification of the relevant parameters, including the diffusivities of the guest molecules in different sample regions as well as their permeability through internal transport barriers and at the interface between the pore space and the surrounding atmosphere. Most importantly, this information is provided non-invasively, without any interference with the intrinsic processes of the sample under study. NMR spectroscopy has thus proven to be particularly qualified to explore the influences of the different phase states of the guest molecules on overall transport, opening novel routes for the transport-optimized design and performance of porous materials.

Particular concern deserve those cases where, initiated by very small changes in temperature or pressure, phase transitions may lead to dramatic changes in the transport properties. This is especially evident for hierarchically structured pore systems. In this way, by transferring the fluid in the mesopores from sub- to supercritical state, the accessibility of the micropores in hierarchically organized porous materials, and hence, e.g., the effectiveness factor of heterogeneously catalyzed chemical reactions, may be dramatically enhanced. A specially interesting route for process design is offered by the experimentally demonstrated fact that a fluid in pores may already
transit to the supercritical phase, while the surrounding, excess fluid is still in the liquid state. Thus, properly designed mesoporous materials can be used to spatially localize regions (possibly hierarchically organized), where by only a tiny change of the external parameters the fluid can be turned into a supercritical one, with all unique properties inherent to it, and vice versa. The design of processes based on such phenomena is notably facilitated by the fact that, irrespective of huge changes in the guest propagation rates within the mesopores, diffusion in the microporous space, i.e., in the region of relevance for the elementary processes of molecular separation and/or conversion, remains essentially unaffected.

Challenges of future research, which most notably will benefit from the potentials of PFG NMR, include (i) the establishment of a comprehensive view on diffusion in mesopores over the whole range of loadings and phases, including the supercritical state, (ii) experiments where transitions into the supercritical state are initiated by changing either temperature or pressure (rather than by coupled changes of both of them as so far generally considered) and (iii) the consideration of all these phenomena for multicomponent guest phases. A close correlation with the ample potentials in a very diverse range of applications including sorption, catalysis, sensors, life sciences, biochemistry and bio-systems.

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