Mass transfer in mesoporous materials: the benefit of microscopic diffusion measurement†

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We introduce the various options of experimentally observing mass transfer in mesoporous materials. It shall be demonstrated that the exploration of the underlying mechanisms is excessively complicated by the complexity of the phenomena contributing to molecular transport in such systems and their mutual interdependence. Microscopic diffusion measurement by the pulsed field gradient (PFG) technique of NMR offers the unique option to measure both the relative amount of molecules adsorbed and the probability distribution of their displacements over space scales relevant to fundamental adsorption science just as for technological application. These advantages are shown to have cared for a recent breakthrough in our understanding. The examples presented include the measurement of diffusion in purely mesoporous materials and the rationalization of the complex concentration patterns revealed by such studies on the basis of suitably chosen micro-kinetic models. As an interesting feature, transition into the supercritical state is shown to become directly observable by monitoring a jump in the diffusivities during temperature enhancement, occurring at temperatures notably below the bulk critical temperature. PFG NMR studies with hierarchical materials are shown to permit selective diffusion measurement with each of the involved subspaces, in parallel with the measurement of the overall diffusivity as the key parameter for the technological exploitation of such materials. We refer to the occurrence of diffusion hysteresis as a novel phenomenon, found to accompany phase transitions quite in general. Though further complicating the measuring procedure and the correlation between experimental observation and the underlying mechanisms, diffusion hysteresis is doubtlessly among the new options provided by diffusion studies for gaining deeper insight into the structure and dynamics of complex porous systems.

1 Introduction

The intimate interaction of molecules with pore surfaces and the option of tailoring these surfaces with respect to both their geometry and chemistry is crucial for the multifold application of nanoporous materials in an ample and continuously growing field of technologies, including mass separation, storage, molecular sensing and conversion.1–4 As a prerequisite of a profitable application of these technologies it has to be ensured that the performance is not excessively impeded by a finite rate of mass exchange between the internal pore volume and the surroundings.5–7 Besides its relevance for fundamental sciences, the investigation of mass transfer in nanoporous materials has thus become a topic of supreme practical importance.8

Conventionally, the transport characteristics of nanoporous materials are explored by recording the rate of molecular uptake following a stepwise change of the concentration of the guest molecules of interest in the surroundings, either by pressure variation or by changing the composition in the surrounding fluid.9 Assuming that the nanoporous material under study consists of quasi-homogeneous particles whose transport characteristics, for a given guest molecule, are adequately described by an (effective) diffusivity, this diffusivity follows in a straightforward way by matching the solution of the corresponding diffusion equation (Fick's 2nd law) to the behavior experimentally observed.7,10

It has to be emphasized that, by recording the response of the system to changing boundary conditions, this type of experiments does indeed adequately and completely correctly reflect the net effect of the phenomena ongoing during the technological application of these materials. Over decades, however, for numerous systems this type of experiments gave rise to the wrong conclusion that the thus-determined (effective!)
diffusivity did correctly represent the diffusivity of the guest molecules in the genuine pore system of this material. In fact, following first “microscopic” measurements of diffusion in zeolitic host-guest systems and the observation of intracrystalline diffusivities exceeding the macroscopically observed ones by several orders of magnitude, a critical reconsideration of the “conventional” experiments revealed that, in many cases, the recorded equilibration rates were controlled by processes different from “intracrystalline” diffusion, i.e. from diffusion in the genuine pore network. Processes responsible for such limitations different from genuine intracrystalline diffusion include the dissipation of the heats of adsorption or desorption and the permeation through additional transport resistances occurring on either the external surface of the nanoporous particles/crystallites or in their (intracrystalline/intraparticle) bulk phase.

These findings were of twofold relevance. First, they have led to a total change of our view on mass transfer in zeolites and related nanoporous materials. The fact that, in some cases, the “new” values of intracrystalline diffusivities did exceed the “old” ones by five orders of magnitude necessitated a reconsideration of the conditions under which the elementary steps of mass transfer were so far assumed to occur. Notably, the new paradigm of mass transfer resulting from these studies is fully supported by the results of quasi-elastic neutron scattering and molecular dynamics simulations which may access truly microscopic dynamics unperturbed by any additional transport resistances. Second, and most importantly from a technological view point, since mechanisms different from diffusion in the genuine pore network were found to be rate determining for the overall mass transfer, efforts for their elimination were recognized as an important route for performance enhancement. This very problem has, in particular, notably contributed to the growing attention of the scientific community towards mesoporous materials, which are the center of this themed issue.

Acceleration of molecular exchange between the space of micropores and the particle surroundings, as the primary objective of mesoporosity for performance enhancement in technological application, may clearly be revealed already by macroscopic diffusion studies, notably in conventional uptake and release measurement. In view of the complexity of the involved phenomena and processes, however, these techniques alone generally fail in providing that amount of information which is necessary for a comprehensive description of the transport phenomena within such materials. Therefore, in complete analogy to the situation encountered with zeolitic materials, access to the internal microdynamics is absolutely essential for giving a deeper insight into the transport properties of mesoporous solids. With its first applications to diffusion studies of fluids in mesoporous materials, PFG NMR has, once again, demonstrated its versatility and its potentials for the investigation of complex systems and, in particular, of fluids under confinement by porous materials quite in general.

These applications are in the focus of the present contribution. After recollecting, in the following two sections, some of the basic laws of diffusion, and of the fundamentals of diffusion measurement quite in general, Section 4 introduces the fundamentals and the procedure of diffusion measurement by PFG NMR. In addition to this introduction, we refer to the ample literature covering the fundamentals of NMR with some of the editions particularly dedicated to diffusion measurement by NMR. Observation and interpretation of the different phenomena of mass transfer occurring in purely mesoporous materials are in the focus of Section 5, while Section 6 deals with materials containing hierarchically organized pore spaces, including mesopores.

2 Basic laws of diffusion

Fig. 1 describes, in a cartoon-like manner, the different situations under which, typically, diffusion phenomena are investigated. Fig. 1a corresponds to the situation of Fick’s classical
**Fig. 1** Schematic representations for the measurement of (a) transport diffusion and of self-diffusion by (b) following the (counter-) flux of differently labeled molecules (red, green) or by (c) recording the displacement of the individual molecules.

**diffusion experiment,**\(^{39,40}\) considering the particle flux evolving under the influence of a gradient of the particle concentration. In the given context, we consider the flux of guest molecules within a network of pores (as indicated by the framework) rather than of a solute (salt) in a solvent (water) as investigated by Adolf Fick in his studies. In both cases, however, near-equilibrium conditions allow the implication of a linear correlation between the particle flux and the gradient of the particle concentration:

\[
  j = -D_T \frac{\partial c}{\partial z} \tag{1}
\]

The factor of proportionality, \(D_T\), is the diffusivity. Considering diffusion in nanoporous materials, the thus-defined diffusivity is generally referred to as the transport diffusivity (indicated by the subscript \(T\)) since, in this case, molecular diffusion does in fact result in a process of net particle transport. Alternatively and in other communities, the thus-defined diffusivity is also referred to as the chemical or collective diffusivity. Note that \(D_T\) is clearly not a function of the concentration gradient, but it can be (and is in most cases) a function of the given concentration.

Combining eqn (1) with the law of mass conservation,

\[
  \frac{\partial c}{\partial t} = -\frac{\partial j}{\partial z} \tag{2}
\]

yields Fick’s 2nd law

\[
  \frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left( D_T \frac{\partial c}{\partial z} \right) \tag{3}
\]

often also referred to as the diffusion equation.

In complete analogy with eqn (1), the correlation between the fluxes of differently labeled molecules and the concentration gradients as exemplified in Fig. 1b may be used for defining a self- (or tracer) diffusivity \(D\):  

\[
  j^* = -D \frac{\partial c^*}{\partial z} \tag{4}
\]

with \(j^*\) and \(c^*\) denoting flux and concentration of one of the two differently labeled molecules. While \(D\) is, in general, a function of the total concentration, it is clearly independent of \(c^*\) (i.e. of the proportion chosen for the different labeling). Since the self- and the transport diffusivities refer to different physical situations, namely to overall equilibrium and to a non-equilibrium situation with a gradient in the overall particle concentration, they cannot be expected to coincide. Since, however, both diffusivities are indications of the omnipresent thermal motion, they should be expected to be correlated. Different model-based approaches for their correlation may be found in the literature.\(^7,41,42\) It is important to note that, in the limit of negligibly small interaction between the guest molecules, both diffusivities coincide. This conclusion can be easily based on the representations in the literature.\(^7,41,42\) Considering the representations in Fig. 1a and b, together with eqn (1) and (4): choosing coinciding gradients for the overall concentration in Fig. 1a and for one of the labeled species in Fig. 1b (which happens to be the case in the given examples), for non-interacting molecules (which “do not know from each other”) also the resulting fluxes have to coincide which, via eqn (1) and (4), leads to coinciding self- and transport diffusivities. This coincidence of self- and transport diffusion for non-interacting diffusants may, quite generally, be understood as a consequence of the fact that it is nothing else than the particle interaction which gives rise to a distinction between equilibrium and non-equilibrium phenomena.\(^43\)

It was in Einstein’s groundbreaking work in the field of diffusion\(^40,44\) published exactly 50 years later than Fick’s paper,\(^39\) that the situation described in Fig. 1c was recognized as an alternative access to the definition of the self-diffusivity, being completely equivalent to the definition based on the procedure illustrated by Fig. 1b in combination with eqn (4). According to Einstein, the mean square value of the displacements \(z\) of diffusing particles in a given direction may be shown to increase linearly with the observation time \(t\):

\[
  \langle z^2(t) \rangle = 2D_t t \tag{5}
\]

where the factor \(D_t\), appearing in this relation as a factor of proportionality between the mean square displacement and the observation time, coincides with the factor of proportionality between particle fluxes and concentration gradients as defined by the application of Fick’s 1st law, eqn (4), for labeled molecules under macroscopic equilibrium. In fact, the equivalence between these two definitions may be easily shown by calculating the mean square displacement, eqn (5), with the probability that, during time \(t\), a diffusing molecule has been shifted over a distance \(z\). This probability results as the solution of the diffusion equation (Fick’s 2nd law, eqn (3)), written now in terms of the concentration of the labeled molecules within a uniform overall concentration:

\[
  \frac{\partial c^*}{\partial t} = D \frac{\partial^2 c^*}{\partial z^2} \tag{6}
\]

where we have made use of the fact that the self-diffusivity is independent of \(c^*\). With the initial condition \(c^*(z,0)\), given by
the Dirac’s delta function (being infinity for \( z = 0 \) and zero elsewhere), one obtains

\[
P(z, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left\{ \frac{-z^2}{4Dt} \right\}. \quad (7)
\]

Since it is exactly this probability which may be determined by PFG NMR, we shall come back to this point in Section 4.

In the subsequent section we are going to provide an overview of the various options for experimentally observing diffusion phenomena in nanoporous materials and of their correlation with the fundamental laws of diffusion just described. For more detailed representations we refer to the review ref. 45, the compilations provided by ref. 8, 46 and 47 and the textbook.7

3 The various options of diffusion measurement with nanoporous materials

The information accessible by experimental observation of diffusion phenomena depends on the correlation between the space scale, over which mass transfer is recorded, and the different lengths characterizing the structural features of the material with relevance for mass transfer. These lengths include (i) the pore size, (ii) the diameter of the nanoporous particles/crystallites containing the pore system and (iii) the diameter of the intergrowths/pellets into which, generally, the individual crystallites are compacted in their technological use. In hierarchical pore spaces, with mesopores traversing the microporous bulk phase, this set of parameters has to be complemented by a further length representing the mean distance which the guest molecules in the microporous space have to cover before getting in contact with the mesopores. Finally, even seemingly homogeneous nanoporous materials are sometimes found to be traversed by intrinsic transport resistances.18–21,48 In such cases, the mean distance between these resistances has to be considered as an additional space parameter of relevance for diffusion.

With respect to the relevant diffusion path length, the techniques of diffusion measurement may be classified into essentially three groups. The first one comprehends techniques which are able to provide information about the elementary steps of diffusion, including the time mean between molecular reorientation or jumps as accessible, e.g., by NMR line shape analysis49–53 and exchange NMR54–56 and dielectric spectroscopy,57–59 and diffusivities over extra-short displacements of a few nanometers maximum as accessible (jointly with information about jump lengths and frequencies) by quasi-elastic neutron scattering (QENS).23,26,60 It is important to note that QENS, depending on the nucleus under consideration, is able to record the coefficients of both self-diffusion and transport diffusion.61–63

The information provided by these techniques does, obviously, refer to space scales which are, in general, notably smaller than the above-considered length parameters. The thus-determined diffusivities do, therefore, provide a valuable standard for comparison with the diffusivities determined with the more macroscopic techniques if, in the material under study, the presence of, e.g., internal barriers or mesopores leads to reduced or enhanced diffusivities. The penalty for having this important option is, however, the fact that the techniques of this class of measurement are insensitive towards transport impairment by internal or external barriers as well as towards mesopore-induced transport enhancement in hierarchical pore systems.

The other extreme of diffusion path lengths is covered by the so-called macroscopic techniques of diffusion measurements. In these techniques, the experiments are initiated by a well-defined change of the pressure in the surrounding atmosphere; information about the transport phenomena is deduced by recording and analyzing the overall effect of this change in the boundary conditions on the system under study. The diffusion path lengths associated with these changes are, obviously, of the order of the spatial dimensions of the bed of crystallites/particles under study. Conventionally,9 macroscopic diffusion measurements are accomplished by an, ideally stepwise, increase or decrease in the surrounding pressure. The relevant transport parameters, notably intracrystalline diffusivities and surface permeabilities, have to be deduced by comparison of the subsequently recorded variation in the loading, i.e. the time dependence of molecular uptake or release, with the dependencies predicted on the basis of the diffusion equation, eqn (3), with the appropriate initial and boundary conditions after integration over the whole space of the nanoporous host. Thus, in an uptake experiment with spherical particles of radius \( R \) with negligible surface resistances and an essentially constant diffusivity over the concentration range considered, e.g., the increase \( m(t) \) of the amount adsorbed results to be

\[
\frac{m(t)}{m(t \to \infty)} = 1 - 6 \pi \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{n^2 \pi^2 D_{\text{T}} t}{R^2} \right). \quad (8)
\]

As a matter of course, this type of experiments does only yield a genuine intracrystalline (intra-particle) diffusivity if the underlying assumption is correct, i.e. if the rate of mass transfer is indeed exclusively determined by intracrystalline diffusion.

More sophisticated techniques of macroscopic diffusion measurement provide the option to obtain further information about possible influences of additional mechanisms on the observed mass transfer phenomena, including reduced heat release or permeation through the surface. The frequency response method7,67–71 e.g., is based on the observation of the phase shift and the intensity in the variation of the guest pressure above the material under study induced by a sinusoidal variation in the volume. Here, depending on the leading mechanisms, characteristic differences in the dependencies of these quantities on the frequency may be observed, all of which again result as solutions of the diffusion equation (eqn (3)) with the relevant boundary conditions.
In the Zero-Length Column (ZLC) method,\textsuperscript{7,72–74} the host system under study is equilibrated at a uniform concentration of the guest molecules contained in an inert gas stream. Here, the diffusion experiment is initiated by switching off the guest concentration in the gas stream. The flow rate has to be chosen high enough to ensure essentially zero guest concentration at the external surface of the particles. Information about intraparticle diffusion is contained in the time dependence of the decaying guest concentration in the purging gas flow, which may be deduced by comparison with the appropriate model considerations, again based on the corresponding solutions of the diffusion equation, eqn (3). In this type of experiments, additional information about possibly corrupting mechanisms may be attained by variation of the flow rate and the nature of the inert gas molecules.

It is true that, in these techniques, external influences – like, e.g., bed resistances or the finite rate of the dissipation of the heat of adsorption – may, to a large extent, be ruled out. However, even in such cases the evidence provided by such conclusions may be hugely obscured if there are significant distributions in the particle sizes and in the magnitude of the transport parameters. Moreover, by their very nature, macroscopic techniques are unable to distinguish between the different mechanisms by which, in complex nanoporous materials, overall mass transfer is determined, including, in addition to micropore diffusion, transport enhancement by mesopores or transport impairment by internal resistances. This situation is illustrated by recent ZLC measurements with mesoporous (“mesostructured”) zeolites of type HZSM-5,\textsuperscript{75} where, by ZLC diffusion measurements, a remarkable reactivity enhancement with increasing mesoporosity is shown to be accompanied by an enhancement of the overall diffusivities. It is remarkable, however, that this enhancement is of the order of not more than 50\%, while in uptake studies with other mesoporous zeolites, including other specimens of mesoporous MFI-type zeolites\textsuperscript{76} and mesoporous SAPO-34,\textsuperscript{77} transport enhancement by several orders of magnitude may be observed. From the uptake rates alone no information about the structural or micro-dynamic origin of these differences is available.

Any distinction between the different mechanisms contributing to mass transfer in nanoporous hierarchical materials is notably facilitated if the diffusion paths recorded in the experiments may be varied from distances notably smaller than the particle diameters up to these diameters. Techniques which are able to provide this type of information are generally referred to as microscopic ones. The pulsed field gradient (PFG) NMR technique of NMR has proved to be an ideal technique obeying exactly this requirement. It operates under equilibrium conditions and, hence, corresponds to the situation illustrated in Fig. 1c. Its fundamentals and the wealth of information about mass transfer in mesoporous materials which, most recently, has been gained with this technique are in the focus of this contribution and shall be dealt with in more detail in the subsequent sections.

In the last decade, with the introduction of interference microscopy\textsuperscript{78} and IR microscopy,\textsuperscript{79} also the counterpart of PFG NMR for microscopic diffusion measurement under non-equilibrium conditions was established in sorption science. These methods, generally referred to as micro-imaging techniques,\textsuperscript{7,45} allow one to record intracrystalline/intraparticle concentration profiles during molecular uptake and release. In this way, for the first time intracrystalline fluxes and, following the scheme given in Fig. 1a, transport diffusivities could be monitored in microscopic measurements. IR micro-imaging, moreover, allows the distinction between different molecular species, including isotopes, so that also microscopic tracer-exchange experiments (and hence the measurements of self-diffusivities – see Fig. 1b) have become possible. In this way, an extensive experimental basis for comparing self- and transport diffusivities could be established.\textsuperscript{80} Examples of the potentials of these techniques of micro-imaging, often complemented by the information provided by PFG NMR self-diffusion measurements, may be found elsewhere.\textsuperscript{45,81,82}

Though there is no doubt that these techniques of micro-imaging have all potentials for notably contributing to our understanding of mass transfer in mesoporous and, in particular, in hierarchical porous materials, experiments are still in the first stage of exploration. It is, therefore, the PFG NMR technique, which is in the center of our contribution. Based on the very first experiments of the last few years, it strives to give an overview of the type of information accessible in this way, on mass transfer in mesoporous materials.

4 Diffusion measurement by pulsed field gradient NMR

4.1 NMR fundamentals

Nuclear magnetic resonance provides direct access to the key data of fluid behavior in the porous space of interest. Most importantly, it is able to simultaneously probe phase-state related quantities and their dynamical properties. Thus, by recording the NMR signal intensity in a sample of a porous solid as a function of the external gas pressure, one is able to measure the respective adsorption isotherm. The adsorption isotherm is known to serve as an indicator of the phase state in the pores.

Simultaneously, in the same sample and under the same conditions, a number of further quantities may be measured. One of them is molecular diffusion. NMR thus proves to be a self-consistent tool for correlating the phase state of the pore fluid with its transport properties. It is intrinsically non-invasive and non-perturbative, allowing monitoring molecular ensembles as they are, without introducing any external disturbances.

To rationalize the principles of NMR at a level, which is sufficient in the context of this contribution, the classical interpretation of nuclear magnetism may most conveniently be used.\textsuperscript{12,33,16,37} According to it, nuclear spins placed in a magnetic field of intensity $B_0$ perform a precessional motion about the direction of $B_0$ with the angular frequency

$$\omega_0 = \gamma B_0,$$

(9)
where $\gamma$ is the nuclear gyromagnetic ratio. Due to their interaction with the external magnetic field, there will be a tiny difference ($10^{-5}$%) between the numbers of spins having projections along and opposite to $B_0$ (Zeeman splitting in terms of quantum-mechanical description), given by the Boltzmann statistics. This difference gives rise to a net equilibrium magnetization along $B_0$. For providing a measurable signal NMR must operate, therefore, with relatively large nuclear ensembles, compared with other spectroscopic techniques. However, the disadvantage of having to ensure the presence of large numbers of nuclei, being typically of the order of $10^{18}$, is, inherently, accompanied by the advantage of acquiring well-averaged quantities.

By the application of an additional radio-frequency field of the resonance frequency $\omega_0$ over a well-defined short interval of time (the so-called 90° or $\pi/2$ pulse), the net magnetization can be turned from the direction of the magnetic field into the plane perpendicular to it. Under this condition, it can most easily be measured by means of a coil whose axis is positioned perpendicular to $B_0$. In this coil, the rotating net magnetization induces a voltage referred to as the NMR signal or, more precisely, the NMR free induction decay (FID) signal. Obviously, the intensity of the FID signal is proportional to the number of nuclei and, hence, to the number of molecules in the sample. This provides a simple means to measure the adsorption isotherm by tracking the FID signal intensity as a function of the given gas pressure. Notably, due to the substantial differences between the densities of the gaseous and adsorbed phases, the thus-measured NMR signal can be assigned to be essentially proportional to the amount adsorbed. A scheme of the experimental realization of this approach, particularly convenient for the investigation of porous materials, is shown in Fig. 2.

Finally, the rates of nuclear magnetic relaxation strongly depend on the physical state of matter. Thus, intra- and intermolecular dipolar interactions in liquids are subject to a strong averaging due to fast rotational and translational molecular motion. This leads to relatively long nuclear magnetic relaxation times and, hence, to long time spans over which an NMR signal may be observed, being typically of the order of seconds. In solid state, however, these interactions give rise to very rapid nuclear magnetic relaxation, on a time scale of a few up to tens of microseconds. By applying appropriate relaxation “filters”, this huge difference in the relaxation rates may be exploited for separating the NMR signals stemming, respectively, from the frozen and liquid phases and, thus, for studying liquid–solid phase transition phenomena in pore spaces. This method is referred to as NMR-cryoporometry.83–85 It may further be complemented by diffusion measurements.86–90

### 4.2 Pulsed field gradient (PFG) NMR

For the measurement of the translational mobility of fluid molecules one exploits the influence of a purposefully created inhomogeneity of the magnetic field on the Larmor frequency $\omega$ of the nuclear spins which is, in general, applied over short intervals of time, as the so-called field gradient pulses.

![Fig. 2 Schematics of an experimental setup for simultaneously tracing the amount adsorbed and the diffusion characteristics of fluids in porous solids.](image)

Today, most of the NMR spectrometers may be complemented by devices allowing the generation of such pulsed field gradients. For rationalizing the measuring principle we realize that, under the application of a magnetic field $B$ linearly increasing in the $z$-direction,

$$B = B_0 + gz,$$

(10)

with eqn (9) the Larmor frequency

$$\omega = \gamma B = \gamma B_0 + \gamma gz$$

(11)

becomes a function of the $z$ coordinate. With the inhomogeneous field held over a time span $\delta$, each spin will acquire a phase

$$\phi = \int_0^\delta \omega(t) dt = \gamma B_0 \delta + \gamma \int_0^\delta g(t) z(t) dt.$$  

(12)

In this way, the position of the diffusing molecules (more specifically, their $z$-coordinate) is encoded in the phase $\phi$ of the precessional motion of the nuclear spins of these molecules.

In basic versions 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 $t$, as exemplified in Fig. 3. As a consequence of the $\pi$ pulse in the Hahn spin echo pulse sequence91 or the two $\pi/2$ pulses in the stimulated echo pulse sequence92 the field gradient pulses may be understood to give rise to phase shifts $\phi$ in opposite directions. Thus, at the end of the second field gradient pulse,
for a non-moving spin the phase encoding due to the first pulse is perfectly compensated by the second one. Due to diffusion, however, re-phasing may be incomplete and there remains a phase difference \( \Delta \phi \) which may be noted as

\[
\Delta \phi = \gamma g \left( \int_0^\delta z(t') dt' - \int_\delta^{\tau+\delta} z(t') dt' \right).
\]

(13)

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 have implied the validity of the short-gradient approximation, \( \delta \ll t \). This allows neglecting the effect of molecular motion during the field gradient pulses. This is in particular justified when the use of ultra-high field gradient strengths \( g \) allows the application of very short field gradient pulses, being much shorter than the time \( t \) between the field gradient pulses. Implementing these field gradient pulses into the Hahn or stimulated-echo pulse sequences, one is able to determine the resulting NMR signal, the so-called spin echo, as a function of the separation \( t \) and intensity \( g \) of the field gradient pulses.

It may be shown that the attenuation \( S(q, t) \) of the spin-echo signal intensity due to molecular diffusion is the Fourier transform of the so-called mean propagator \( P(z, t) \)

\[
S(q, t) = S(0, t) \int P(z, t) e^{i q z} dz.
\]

(14)

\( P(z, t) \) is nothing else than the mean value of the probability that, during time \( t \), a molecule is shifted over a distance \( z \), i.e. of exactly this quantity which, with eqn (7), we have met already in Section 2 on considering mass transfer following Fick’s diffusion laws. The average is to be taken over all molecules (spins) within the sample. In eqn (14) we have followed, for brevity, the convention to use the notation \( q = \gamma \partial g \) which is sometimes referred to as the scattering wave-number (or, more generally, wave-vector if the vector form is used). \( S(q, 0) \) in eqn (14) is the signal intensity in the absence of the magnetic field gradient pulses.

Inserting eqn (7), the propagator for unrestricted, normal diffusion, into eqn (14) yields a spin-echo attenuation of exponential form

\[
S(q, t) = S(q, 0) \exp(-q^2 Dt).
\]

(15)

With eqn (15), the diffusivity (and hence, via eqn (5), the mean square displacement in the direction of the magnetic field gradient applied) may be easily determined from the slope of the semi-logarithmic representation of the intensity of the NMR signal versus \( q^2 t \).

For estimating the diffusion path lengths thus observable, we imply, that as a prerequisite for a sufficiently reliable measurement of the signal attenuation as given by eqn (15), the exponent \( q^2 Dt \) has to be of the order of or larger than 1. With eqn (5), with typical maximum values of \( g = 25 \text{ Tm}^{-1} \) for the amplitude and of \( \delta = 2 \text{ ms} \) for the width of the field gradient pulses and with the gyromagnetic ratio \( \gamma_{1H} = 2.67 \times 10^8 \text{ T}^{-1} \text{ s}^{-1} \) for protons as the usually considered nucleus, the mean value of molecular displacements is found to be of the order of 100 nm. The attainable minimum diffusivities depend on the observation time which is controlled by the nuclear magnetic relaxation times of the guest molecules. Under favorable conditions, observation times of seconds are possible which, with eqn (5), would correspond with minimum diffusivities of the order of \( 10^{-14} \text{ m}^2 \text{ s}^{-1} \). With reference to the minimum displacement, as a consequence of their smaller gyromagnetic ratios \( \gamma_{13C} = 0.67 \times 10^8 \text{ T}^{-1} \text{ s}^{-1} \), \( \gamma_{129Xe} = 0.75 \times 10^8 \text{ T}^{-1} \text{ s}^{-1} \), \( \gamma_{15N} = 0.27 \times 10^8 \text{ T}^{-1} \text{ s}^{-1} \), the measuring conditions deteriorate for other probe nuclei, yielding values larger by a factor of 4 for carbon and xenon and of even 10 for nitrogen.

Eqn (15) may also be applied as a useful approximation if molecular propagation deviates from normal, unrestricted diffusion. In such cases, the quantity \( D \) has to be interpreted as an “effective” (or “apparent”) diffusivity, defined by the relation

\[
D_{\text{eff}} = \langle \bar{z}^2(t) \rangle / 2t,
\]

(16)

which, formally, coincides with the Einstein relation, eqn (5). In this way, under the condition of normal diffusion, the effective diffusivity is ensured to coincide with the self-diffusivity. Quite generally, i.e. for any type of internal diffusion characteristics, eqn (15), with \( D \) replaced by \( D_{\text{eff}} \), holds exactly in the limit of sufficiently small intensities of the field gradient pulses \( q \to 0 \).

In a nanoporous host–guest system, molecular diffusion must be considered to occur in quite different regions, including the intra- and intercrystalline/particle spaces and, in hierarchical pore systems e.g., even different pore spaces within one and the same crystallite/particle. Several approaches describing the PFG NMR signal-attenuation in complex systems with different internal diffusivities may be found in the literature.

For the discussion in the present communication, we confine ourselves to two limiting cases, namely those of slow and of fast molecular exchange between the regions of different diffusivities. In the first case, over the total observation time \( t \), all individual molecular trajectories can be assumed to remain in a particular one of these regions. Then the PFG NMR signal attenuation results to be

\[
S(q, t) = S(q, 0) \sum_i p_i \exp(-q^2 D_i t)
\]

(17)

with \( p_i \) and \( D_i \) denoting, respectively, the relative populations and diffusivities of the different region. For simplicity, differences in the influence of nuclear magnetic relaxation, accounted for by \( S(q, 0) \), in the different regions are assumed to be negligibly small.

As a prerequisite of the opposite limiting case of fast molecular exchange, molecular life-times in the different regions must be much smaller than the observation time. In this case, the PFG NMR attenuation curve assumes the shape of an exponential as given by eqn (15), now with the effective diffusivity

\[
D_{\text{eff}} = \sum_i p_i D_i
\]

(18)

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resulting as the mean of the molecular diffusivities in the
different regions. The diffusivities \( D_i \) are calculated \( \text{via} \) eqn (5)
by considering the vector sum of the displacements and the
sum of the residence times separately for each individual
region \( i \).

We recollect that 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, up 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 systems\(^{95} \) or for strongly
confined fluids,\(^{7} \) while the latter displacements are typical of
gas phase applications.\(^{96} \) Recalling that the main scope of the
present work is fluid transport in mesoporous solids, it is worth
noting that thus the molecular displacements of fluids traced
using PFG NMR substantially exceed typical pore dimension
and, in most cases, the typical correlation lengths of meso-
porous materials (except for hierarchically organized materials
with long-range correlation in the pore structure). Therefore, as
a consequence of the central limit theorem,\(^{97} \) guest diffusion in
mesoporous materials is, on the time and space scales of PFG
NMR experiments, adequately described by a Gaussian propa-
gerator, \textit{i.e.} by eqn (7), though now with an effective diffusivity.
At pore saturation (and by assuming that the pore sizes are
large enough to ensure that molecular microdynamics is as in
the bulk fluid), the effective diffusivity may be noted in the
simple form\(^{7,98,99} \)

\[
\text{Eqn (19) }
\]

where \( D \) is the diffusivity of the pore fluid in the bulk \( \text{i.e.} \) in
unconfined space) and the tortuosity factor \( \tau > 1 \) takes account
of the detours in the trajectories of the molecules caused by the
confinement due to the pore walls.\(^{100} \)

Phase equilibria and molecular diffusion may be investi-
gated using a setup shown in Fig. 2 by the following procedure.
First, the pressure in a reservoir, which has a volume substan-
tially exceeding that of the NMR sample, is set to a desired
value by connecting it to a flask containing the liquid under
study or to a turbo-molecular pump. Subsequently, the reser-
voir is brought into contact with the NMR tube containing the
porous material under study until equilibrium is established.
The equilibration process may be monitored by recording
the NMR FID signal. Subsequently, guest self-diffusivities are
measured by application of the PFG NMR pulse sequence.
These steps are repeated with any gas pressure in the reservoir.

The adsorption isotherm (in relative units) is obtained by
normalizing with the FID intensity determined with a suitably
chosen external pressure \( P \), most conveniently with a pressure
of about 98% of the saturation pressure for avoiding condensa-
tion of the bulk fluid.

For facilitating diffusion measurements at different tem-
peratures, sometimes the loaded PFG NMR sample tubes are
fused. As long as the total amount of guest molecules in the free
space of the sample tube remains negligibly small in com-
parison with the amount in the pore space, such procedure
provides an easy means for measuring the temperature depen-
dence of diffusion for a given loading. Temperature variation in
such systems is subject to the conditions of conventional
isosteric sorption measurements,\(^{1,65} \) with the guest pressure
inside the sample tubes increasing with increasing temperature,
following the Boltzmann dependence with the isosteric
heat of adsorption in the exponent.\(^{7,101,102} \) We shall come back
to this consideration when discussing, in Section 6.3, the PFG
NMR self-diffusivity data for guest molecules in hierarchical
zeolites.

5 Diffusion in mesopores

On considering mass transfer in mesoporous materials, one
must be aware of the fact that the guest molecules, as in
the bulk phase and notably deviating from their behavior in
microporous materials, may occur in different phase states.
Indeed, molecular mobilities in gases, liquids and solids
dramatically differ from each other. In confined systems,
different phases may spatially coexist with each other. This
may lead, in conjunction with alternating periods of migration
in both phases in the molecular trajectories, to severe modi-
fications of the transport mechanisms. The latter result, in
particular, due to the existence of interfaces between the
domains of different phases. Quite generally, the trajectories
may include periods of surface diffusion, diffusion in multi-
layers on the pore walls and diffusion through the pore space.
Some generic patterns of molecular propagations in the pore
spaces of mesoporous solids are, in a cartoon-like manner,
exemplified in Fig. 4.

The investigation of solid–liquid equilibria is a particularly
challenging task of fundamental research.\(^{104,105} \) Moreover, in
this way most important information about the internal pore
connectivity may be obtained which is scarcely accessible by
other techniques.\(^{98,99,106,107} \) During their technological exploitaion,
however, mass transfer in mesoporous materials generally occurs in coexisting liquid and gaseous phases. It is, therefore, this situation which shall be in the focus of our presentation. Before, in the subsequent sections, the different mechanisms of transport shall be discussed in more detail, we are going to present an informative example in which most of the relevant features of mass transfer in such materials may be recognized.

As such an example, Fig. 5 shows the diffusivities of cyclohexane measured using PFG NMR in Vycor porous glass during gas pressure variation in the surrounding atmosphere. We recollect that each experimental point in the upper part, representing the amount adsorbed at a given external pressure on either the adsorption or desorption branch, is provided by the intensity of the FID signal. Each of the diffusivities represented in the lower part results from the best fit between a complete PFG NMR attenuation curve $S(q,t)$ recorded at the given external pressure with its theoretical dependency as given by eqn (15).

The figure shows quite a complex behavior which turns out to be generic for mesoporous materials quite in general, irrespective of their fine structure. Starting from zero loading one observes, with increasing external pressure, (i) a strong increase in the diffusivities, (ii) the formation of a maximum at intermediate pressures and (iii), finally, at capillary condensation, an essentially constant value of the diffusivities. On decreasing pressure, over the range of capillary condensation, the diffusivities are found to notably deviate from those observed at the same external pressures during adsorption, exhibiting, as a feature, (iv) a pronounced hysteresis in the diffusivities. In the following sections we are going to correlate these features with their microdynamic and microstructural origin.

5.1 Surface diffusion

In the range of sub-monolayer coverage, which is attained if the porous material under study is brought into contact with a gas atmosphere at relatively low pressures, the dominating mechanism of mass transfer through porous solids is surface diffusion. Indeed, in this regime the intrapore population consists almost exclusively of the molecules physisorbed on the inner surfaces of the porous solid. Due to the relatively low energies of physisorption, the thermal energy of these molecules is high enough to give rise to a thermally-activated hopping of the molecules along the surfaces.

Fig. 6 shows surface diffusivities of $n$-heptane measured in Vycor porous glass by means of the PFG NMR technique. The diffusivities are plotted as a function of the surface coverage $c$, which is defined as $c = \theta/\theta_m$, where $\theta$ is the total amount adsorbed and $\theta_m$ is the amount adsorbed corresponding to coverage by one monolayer. As a remarkable result, the diffusivities are seen to increase with increasing surface coverage. This finding is in a striking contrast to the diffusion of adatoms on metal surfaces, which typically shows the exactly opposite behavior, namely diffusivities decreasing with increasing surface loading. Such a behavior is easily referred to the increasing resistance by other adatoms, experienced by a particular one on its trajectory along the surface. The completely different behavior observed with sub-monolayer coverages on mesoporous materials would, therefore, point to a completely different microdynamic situation.

Before following this line of arguing in further detail, we are going to exclude that, in addition to surface diffusion, other modes of molecular transport might notably contribute to the measured diffusivities, giving rise to the unexpected increase with increasing surface coverage. This might, in particular, concern the possibility that molecular flights through the free space within the pores lead to such an acceleration. In order to clarify this issue, we are going to apply a procedure which is based on the application of the Einstein relation, eqn (5),
for composed systems and which shall also be used further on in this contribution.

Let us consider a molecular trajectory composed of periods of erratic hops along the inner surface of the porous material and of flights through the free space of the pores. Due to the low pressure in the gas phase and the small pore dimensions, being of the order of nanometers, mutual encounters of the molecules in the gas phase may be excluded. Since the displacements recorded by the PFG NMR diffusion measurements may be assumed to be much larger than any correlation length within the pore system and, clearly, also the pore diameters, the observed transport phenomena are completely adequately described by normal diffusion with an (effective) diffusivity given by the relation

\[ D = \frac{1}{6t} \left( \left( \sum_{i} \hat{s}_{s,i} \right)^2 + \left( \sum_{j} \hat{s}_{g,j} \right)^2 \right), \tag{20} \]

where \( \hat{s}_{s,i} \) and \( \hat{s}_{g,j} \) denote the individual steps of displacement on the surface (“hops”, subscript s) and in the free pore space (“flights”, subscript g). Differing from the notation of eqn (5) referring to only one direction, eqn (20) considers displacements in three-dimensional space so that the pre-factor has now become 6 rather than 2.

Since displacements in the pore free space and on the surface are uncorrelated, all cross terms in eqn (20) are annihilated by the averaging procedure yielding

\[ D_{\text{eff}} = \frac{1}{6t} \left( \left( \sum_{i} \hat{s}_{s,i} \right)^2 \right) + \frac{1}{6t} \left( \left( \sum_{j} \hat{s}_{g,j} \right)^2 \right). \tag{21} \]

The first term on the right-hand side of eqn (21) refers to displacements along the surface and may be represented, therefore, in terms of a surface diffusivity \( D_{s} \) by using the defining equation \( \left( \sum_{i} \hat{s}_{s,i} \right)^2 = 6D_{s}t_{s} \). Likewise, the second term may be represented by the analogous expression \( \left( \sum_{j} \hat{s}_{g,j} \right)^2 = 6D_{g}t_{g} \) for the gas phase in the pore space, where the diffusivity \( D_{g} \) may be approached by the Knudsen relation \( D_{K} = \frac{1}{3}d \bar{v} \),

\[ D_{K} = \frac{1}{3}d \bar{v}, \tag{22} \]

for flights in a tube of diameter \( d \), notably exceeding the size of the molecules, as a prerequisite of its unambiguous application, with \( \bar{v} \) denoting the average molecular velocity. \( t_{s} \) and \( t_{g} \) denote the mean total times during which, on their trajectories, the guest molecules are, respectively, on the surface and in the free pore space.

With these replacements, eqn (21) may be noted as

\[ D = \frac{t_{s}}{t} D_{s} + \frac{t_{g}}{t} D_{g} = p_{s} D_{s} + p_{g} D_{g}. \tag{23} \]

The second equation is a consequence of the detailed balance equations \( p_{s} = \frac{t_{s}}{t} \) and \( p_{g} = \frac{t_{g}}{t} \), correlating the fraction of molecules in a given state with their mean life time in this state.

We note that, in this way, we have reproduced the fast-exchange relation, eqn (18), of PFG NMR.

By straightforward calculations, the relative amount \( p_{g}(1 - p_{s}) \) of molecules in the pore free space may be found to be

\[ p_{g} = \frac{1 - \theta z P_{0} M}{\theta \rho_{s} R T}. \tag{24} \]

where \( z = P/P_{0} \) is the relative pressure, \( M \) the molar mass of the guest molecules, \( \rho_{s} \) the guest density in the liquid state, \( R \) the universal gas constant, and \( T \) the temperature. The highest fraction \( p_{g} \) in the range of sub-monolayer coverage is expected to be attained at \( \theta \approx \theta_{w} \). With \( P_{0} = 6.6 \text{ kPa at } T = 300 \text{ K, and with } M = 0.1 \text{ kg mol}^{-1} \) and \( \rho_{s} = 0.68 \text{ g cm}^{-3} \) for n-heptane, \( p_{g} \) is estimated to be \( 2.5 \times 10^{-4} \). Further, with \( v \approx 250 \text{ m s}^{-1} \) at 300 K and \( D_{s} \) given by eqn (22), the upper limit \( p_{g} D_{g}/D_{s} \) of the contribution of gas phase diffusion to overall diffusion is estimated to be of the order of \( 10^{-10} \text{ m}^2 \text{ s}^{-1} \), which is notably smaller than the value of \( 7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) determined for the overall diffusivity under such conditions. Moreover, with decreasing surface coverage and/or external gas pressure the ratio \( p_{g} D_{g}/D_{s} \) may be expected to further decrease. With \( p_{g} \ll 1 \) and \( p_{g} + p_{s} = 1 \), \( p_{s} \) is seen to be, essentially, equal to 1, so that the diffusivity data of Fig. 6 are in fact seen to represent the diffusivity of the guest molecules on the inner surface of the mesoporous material under study.

Having excluded any corruption of the diffusivity data by mass transfer in the gas phase, the remarkable increase of the diffusivities with increasing surface coverage as shown in Fig. 6 can now unequivocally be referred to a pronounced surface heterogeneity. This heterogeneity appears in a distribution of the activation energies which the hopping molecules have to overcome on their trajectories on the pore surface, originating from structural defects on the surface and/or chemical disorder. The solid line shown in Fig. 6 exemplifies the result of an analytical estimate of the diffusivity along a surface with strong energetic heterogeneity, where any correlation between the energy of neighboring sites is excluded.

In Fig. 7, the diffusivity data of Fig. 6 are plotted as a function of the reciprocal temperature. They are seen to nicely follow an Arrhenius dependence

\[ D_{s} = D_{0} \exp\left\{ - \frac{E_{a}/RT}{3} \right\}, \tag{25} \]

with the activation energies shown in Fig. 8. The activation energies are found to decrease with increasing loading. This finding is in complete agreement with our model considerations in which the first molecules are expected to reside on the strongest adsorption sites. With increasing loading, sites of decreasing sorption energy shall be progressively occupied leading to the observed decrease in the activation energies of diffusion.

It is worth noting that surface diffusivities increasing with increasing loading have also been observed with other mesoporous materials, including mesoporous silicon. We have, in particular, recognized (and, thus, rationalized!) the concentration dependence as revealed by our introductory...
5.2 Diffusion under the conditions of multi-layer adsorption

With further pressure increase in the surrounding gas phase, also the relative amount \( p_g \) of molecules in the gas phase increases and, hence, also the contribution of displacements through the free pore space to the overall diffusivity as represented by the second term on the right-hand side of eqn (23).

Having in mind that the absolute number of molecules in the free pore space is negligibly small in comparison with the amount of molecules in the multi-layer \( (p_g < p_s) \) and, hence, \( p_s \approx 1 \), combining eqn (23) with eqn (22) and (24) yields

\[
D_{\text{eff}} = D_m + \frac{(1 - \theta)^{3/2} \zeta P_0 M d^5}{\theta \rho_1 RT} \frac{1}{3},
\]

where the diffusivity in the multilayer is approached by the molecular diffusivity \( D_m \) of the capillary-condensed liquid in the pore space. The reduction of the free pore space and, hence, of the Knudsen diffusivity, with increasing pore filling, is taken account of by using the effective diameter \( (1 - \theta)^{1/2} d \) in place of the genuine pore diameter itself, the use of which was strictly correct only in the limit of negligible loading.\(^\text{124}\)

With eqn (26), the opposing tendencies in the pressure dependence of the second term of eqn (23) and, hence, in the contribution of gas phase diffusion to overall diffusion, become obvious. On the one hand, for BET-type adsorption isotherms the external pressure is known to increase faster than the loading, leading to an increase of \( z/\theta \) with increasing pressure. The term \((1 - \theta)^{1/2}\), however, gives rise to the opposite dependency which becomes the more pronounced the larger the loadings are until, at complete pore filling (capillary condensation; \( \theta = 1 \)), there is clearly no gas phase anymore within the pores and, hence, no gas phase contribution to pore diffusion.

The fluid within the pores has, eventually, attained the state in which its diffusivity may be represented in the form of eqn (19), \( i.e. \) by the diffusivity in the neat fluid, reduced by a “tortuosity factor” which is determined by the pore space geometry. It is exemplified by the data shown in Fig. 5 that further increase in the external pressure does not lead to any perceptible changes in the measured diffusivities.

By inserting the analytical expression of the relevant adsorption isotherms into eqn (26), it is possible to determine for which external pressures and pore loadings the overall diffusivity attains its maximum values. It is shown in ref. 117 that the behavior as exemplified by Fig. 5 is in complete agreement with such estimates.

5.3 Diffusion hysteresis

By eqn (26), the overall diffusivity can be referred to the relative populations of the different phase states within the nanoporous host–guest system and their local diffusivities. As an immediate consequence of the celebrated phenomenon of sorption hysteresis, these relative populations, \( i.e. \) the fractions \( p_l \) and \( p_g \) of molecules in the liquid and gaseous states, are known to be not only a function of the external parameters but also of the sample history. Hence, solely this fact would explain already the formation of a hysteresis loop in the diffusivities as shown in Fig. 5b when the diffusivities are plotted \( \text{versus} \) the gas pressure. If this route of reasoning on the basis of eqn (26) were sufficient, the hysteresis loop in the diffusivities must be expected to vanish if, using the correlation between the gas pressures and relative loadings provided by Fig. 5a, the diffusivities were plotted as a function of the relative pore filling.

In Fig. 9 the diffusivities displayed in Fig. 5b are re-drawn in exactly this way. It becomes immediately visible that the diffusivities on the adsorption and desorption branches do still notably differ from each other. Irrespective of a fast exchange between all states of mobility within the system as substantiated by the large diffusivities and the displacements over micrometers associated with them, and irrespective of the fact that they are now referred to identical overall loadings, guest diffusivities still exhibit pronounced differences. In addition to simple adsorption from the empty state and desorption from
complete saturation, in some cases the actual state of the investigated samples was also attained by following adsorption or desorption from partially loaded states and by an even more complex variation of the pressure back and forth (by performing the so-called scanning experiments\(^{125}\)).

The “history” seen by the sample before establishment of a particular final (average!) loading is thus seen to determine the overall guest diffusivities.\(^{126}\) For rationalizing this behavior we have to explore the origin of the obvious differences in the fluid distribution for one and the same overall density after different sample histories. As one of the key points one may identify that, upon desorption, the liquid-filled regions are expanded. Such a behavior is exemplified by Fig. 10, which shows the diffusivity of cyclohexane in mesoporous silica (PIB-IL\(^{127,128}\)) plotted as a function of the guest density. After attainment of capillary condensation, upon pressure reduction complete pore filling was seen to be maintained over quite a substantial pressure range. This was accompanied by a notable decrease in the guest density. As a counterpart of the decreasing density, the effect of the “stretching” of the pore liquid appears in a remarkable increase in the guest diffusivities.

Stretching of the pore fluid is only possible on the desorption branch and does not occur during adsorption. On comparing the diffusivities for one and the same amount of guest molecules during adsorption and desorption, one must be aware that the fluid stretching on the desorption branch gives rise to two differences, namely a higher diffusivity within the pore liquid and a decrease in the total free volume within the pore space as soon as the pore filling becomes incomplete. Though, as illustrated by Fig. 10, the diffusivity in the stretched liquid does in fact exceed that in the dense liquid, it is still very much smaller than the contribution of the gaseous phase to overall diffusion. As a consequence, the larger volumes occupied by the gaseous phase during adsorption must be expected to lead, for a given total amount adsorbed, to notably larger overall diffusivities than during desorption. This expectation is in complete agreement with the experimental evidence provided by Fig. 9.

Besides this general tendency in the “history dependence” of the diffusivities for a given overall guest concentration, one has clearly to be aware of further influences related to differences in the guest distribution within the porous space. Different geometric configurations of the domains containing capillary-condensed and gaseous phases will also give rise to differences in the respective diffusivities. They may be referred to differences in both the chord-length distributions in the gaseous domains (indicating differences in the Knudsen diffusivities to be expected following eqn (22)) and the density of phase boundaries within the pore space which may give rise to additional transport resistances. The latter influence most informatively appears in the differences in the diffusivities in the freezing and melting branches in mesoporous materials on their solid–fluid phase transition if the diffusivities are plotted for identical fluid phase fraction and referred to the same pressure \(P_s\) of the free liquid and a pressure \(P (\leq P_s)\) which, on the desorption branch, is still big enough for maintaining capillary condensation.\(^{129}\)

**Fig. 10** Diffusivity of capillary-condensed cyclohexane in mesoporous silica (PIB-IL) at 297 K plotted versus the relative density \(\rho_c/\rho_l\) with \(\rho_c\) and \(\rho_l\) denoting the densities of the capillary-condensed liquids at the saturation pressure \(P_s\) of the free liquid and a pressure \(P (\leq P_s)\) which, on the desorption branch, is still big enough for maintaining capillary condensation.\(^{129}\)

It is important to note that the diffusivities measured within these ranges of phase transition remain constant over the laboratory time scale (i.e., notably, over days) if the external parameters are kept constant – differing from each other depending on the system’s “history”. As unveiled by the constancy of the measured diffusivities, the different guest configurations attained via their different histories are thus found to remain “arrested” over essentially unlimited intervals of time, with the overall diffusivity identified as a sensitive probe of the given state of the confined liquid. Different states emerge from the different system histories and represent different out-of-equilibrium distributions of the fluid within the pore network. Being separated by large barriers in the system’s free energy, these states are observed to remain stable.

**Fig. 9** Effective diffusivities of cyclohexane in Vycor porous glass measured using PFG NMR at 297 K as a function of the amount adsorbed, \(\theta\). Different symbols refer to different pathways of the system preparation, namely triangles to continuous pressure increase (data of the “adsorption branch” shown in Fig. 5b, re-plotted), circles to continuous pressure decrease (data of the “desorption branch” shown in Fig. 5b, re-plotted) and all other symbols to a more complex history where the given pressure has been attained by adsorption/desorption (desorption/adsorption) cycles with pressures remaining within the hysteresis loop.\(^{126}\)
over very long intervals of time: the time constant of their relaxation towards the overall minimum in the free energy itself is seen to diverge to infinity with increasing time.\textsuperscript{27}

With the reversibility of the adsorption isotherm at the low gas pressures, indicating the attainment of equilibrium, and its irreversibility at the intermediate pressures, revealing a strong non-equilibrium nature of the adsorption hysteresis, which is further supported by hysteresis in microdynamics, it turns out that this system under study provides a unique option to address the relationship between the data of macroscopic (uptake) and microscopic (PFG NMR) measurements.\textsuperscript{27,131} Such relationship may be established on the basis of Fig. 11, showing the uptake kinetics measured upon stepwise changes of the external gas pressure in two regions corresponding to the reversible and irreversible parts of the sorption isotherm. In addition, the figure displays the predictions of the macroscopic theory by assuming that the equilibration process is solely controlled by diffusive microdynamics, namely the solution of eqn (6) (leading, for spherical particles, to eqn (8)) where we imply that the independently measured self-diffusivities \( D \) of Fig. 5 provides a reasonable estimate.

Remarkably, such a comparison does even yield quantitative agreement. With reference to Fig. 1 we may state that the pressure step did indeed lead to an instantaneous increase of the concentration of molecules at the boundary of the porous particle. Moreover, the molecular fluxes thus created according to eqn (1) happen to coincide, for one and the same concentration gradient, in the system under study, with those given by eqn (4), indicating essentially coinciding transport diffusivities (as relevant for molecular uptake and release) and self-diffusivities (resulting from the PFG NMR measurements). Thus, the molecular diffusivities obtained by a proper analysis of the macroscopic uptake data turn out to be identical with those directly measured using the microscopic PFG NMR technique. In the hysteresis regime, however, diffusion theory completely fails to predict adsorption kinetics. Indeed, it is complex thermodynamics rather than simple molecular rearrangement under quasi-equilibrium conditions by which, in this regime, the system evolution is determined.\textsuperscript{27,132}

### 5.4 Diffusion in supercritical phases

Among the conceptual features of mass transfer in mesoporous materials one important item has been left, so far, out of our discussion, namely the formation of supercritical phases in confined spaces. Though the conditions of their occurrence and the options of their exploitation are still far from being completely understood, diffusion studies appear to have all potentials to contribute to this issue.\textsuperscript{133,134}

We are going to demonstrate these options by considering the system which has been, already, in the focus of our previous discussions, namely Vycor porous glass, contained in a closed vessel and over-saturated by liquid \( n \)-pentane. By heating the system up to 350 K one expects to obtain an Arrhenius-type increase of the intrapore fluid diffusivity. The activation energy for diffusion almost coincides with that of the bulk liquid. This is directly seen in Fig. 12, where both intrapore and bulk diffusivities are shown. However, around a temperature of about \( T = 438 \, \text{K} \) the diffusivity of the intrapore liquid is seen to experience a jump, with no appreciable change with further increasing temperature, appearing in the formation of a plateau.\textsuperscript{133}

Notably, the diffusivity of the bulk liquid does not show, in this temperature range, any visible deviations from the Arrhenius behavior. It is not before \( T = 470 \), which is known to be the critical temperature for bulk \( n \)-pentane, when the diffusivity in the bulk is seen to deviate from the Arrhenius dependence and to jump to much larger values. These two items of experimental evidence unequivocally indicate the formation of the supercritical phase in the mesopores at temperatures substantially below the bulk critical temperature. In the supercritical state, the pore diffusivity remains essentially constant, in complete agreement with the behavior expected by exploiting the Knudsen relation, eqn (22), as an order-of-magnitude estimate since the mean free path remains essentially unchanged which is as well true for the mean velocity,
which increases only in proportion to the square root of the temperature.

These studies did not only provide immediate evidence of the shift of the pore critical temperature by directly measuring the transport properties (the diffusivity) of the confined fluid. By giving absolute numbers for the diffusivities, studies of this type may also attain immediate technological relevance, e.g. by exploiting the option of “triggering” dramatic changes in the pore space diffusivities by only faint changes in the temperature.

6 Diffusion in hierarchical pore spaces

As a consequence of their application as loose particle beds and compacted solids, with essentially the very beginning of their industrial use and their discovery as fascinating and important objects of fundamental and applied research, zeolites, like nanoporous materials quite in general, were applied under conditions where mass transfer of guest molecules proceeds in at least two different spaces, namely in the nanoporous space within the individual crystals/particles and in the surrounding, external meso/macroporous space. There clearly exist simple means to discriminate which one of these mechanisms, in a given case, is the governing one, with the variation of the bed depth in transient uptake/release experiments as one of these options. However, before comparative PFG NMR studies of intracrystalline zeolitic diffusion did yield much larger values than previously assumed, it was common practice to neglect any significant mass transfer resistance due to diffusion in the intercrystalline space if the use of extremely “deep” beds is avoided. It is noteworthy that also first PFG NMR measurements of diffusion in zeolites (water in beds of NaX-type crystallites) failed to make this distinction. Only a couple of years later when, by the use of sufficiently large field gradient pulses, this type of measurement has become possible, with the very first measurements of true intracrystalline diffusivities it turned out that these old data did refer to “long-range” rather than to intracrystalline diffusivities.

Deviating, however, from the situation typically observed with hierarchical pore systems which we are going to consider in more detail in this section, mass transfer in beds of nanoporous particles may be easily represented by two resistances acting in series with each other. They can be quantified by the respective time constants (“first statistical moments”) of molecular uptake or release, which may be represented in the form

\[ \tau_{\text{intra}} = \frac{R^2}{15 D_{\text{intra}}} \]  

(27)

\[ \tau_{\text{bed}} = \frac{L^2}{3 p_{\text{inter}} D_{\text{inter}}} \]  

(28)

with \( R \) and \( L \) denoting, respectively, the mean crystal radius and the bed thickness and with the diffusivities \( D_{\text{intra(inter)}} \) in the intra- and intercrystalline spaces. \( p_{\text{inter}} \) denotes the relative number of guest molecules in the intercrystalline space.

For simplicity, in these relations the influence of any further transport resistances (such as surface barriers) has been neglected. The overall time constant results as the sum of these two terms. In many practical cases, overall mass transfer is seen to be limited by one of these processes, i.e. mass transfer in the individual crystallites (particles, eqn (27)) or in the intercrystalline (gaseous) phase (eqn (28)). Note that both effective diffusivities are directly accessible by PFG NMR. For the measurement of \( D_{\text{intra}} \) the time interval \( t \) between the two gradient pulses (see Fig. 3) must be chosen to be short enough so that the majority of the molecular displacement during \( t \) is unaffected by the crystal surface (i.e. for root mean square displacements \( \sqrt{\langle z^2(t) \rangle} \ll R \)).

\[ D_{\text{l.r.}} = p_{\text{inter}} D_{\text{inter}} \]  

(29)

results as the effective diffusivity observed by PFG NMR as soon as the displacements during \( t \) are sufficiently large (\( \sqrt{\langle z^2(t) \rangle} \gg R \)) and the observation time \( t \) notably exceeds the intracrystalline lifetime \( \tau_{\text{intra}} \) (which, as a consequence of the short molecular life times in intercrystalline space, coincides with the intercrystalline exchange time under the conditions of gas phase adsorption). With these conditions in mind, the product \( p_{\text{inter}} D_{\text{inter}} \) is generally referred to as the long-range diffusivity \( D_{\text{l.r.}} \).

Besides the crystal diameter as a measure of the maximum intracrystalline displacements, there did not exist any independent standard as a criterion for checking the validity of the intracrystalline diffusivities. The situation with the long-range diffusivities was completely different. Following the same reasoning, as illustrated in Sections 5.1 and 5.2 for the contribution of gas phase diffusion to overall mass transfer, it is also possible to predict the magnitude of the long-range diffusivities. Here, the relative amount of molecules in the intercrystalline space follows from the adsorption isotherm and the bed porosity, while the intercrystalline diffusivity can be approximated by means of eqn (22) where the parameter \( d \) is understood as an effective free flight path which may be estimated by reciprocal addition of a mean cord length in the intercrystalline (macro)- pore space and the mean free path in the bulk gas phase. In the process of clarifying the origin of the huge discrepancies between the messages of PFG NMR and of conventional uptake and release measurements on intracrystalline diffusion, the agreement of such estimates with the PFG NMR data on long-range diffusion did provide most important support of the validity of the NMR data.

In Section 6.1 we are going to demonstrate that this principle of determining the overall diffusivity via eqn (29) nicely applies to compacted particles. It shall be seen that the technology-relevant transport is exclusively controlled by the rate of mass transfer in the intercrystalline space and, notably, the fraction of molecules residing there, while the rate of mass transfer in the individual crystalline compartments is seen to be of no influence. As a quite general feature of such type of materials, domains of small pore sizes (namely the nanoporous crystallites) are imbedded in a continuum with notably larger pore sizes.
In all further sections of this review, we shall consider exactly the opposite case where domains with larger pore sizes are imbedded in a continuum with notably smaller pore sizes. In all these systems, the contribution of the different modes of molecular propagation to overall mass transfer is facilitated by considering the respective trajectories, i.e. possible diffusion paths covering the different pore spaces. In this way it shall be illustrated why the contribution of the different pore spaces to overall mass transfer is highly sensitive to the mutual arrangement of these spaces in the material topology. In one case (Section 6.2), we are going to consider mass transfer in a material containing large pores dispersed in a continuum of small mesopores. Subsequently, we are considering a network of large (meso-) pores traversing a continuum of micropores (Section 6.3). Continuing the presentation of Section 5.3 for purely mesoporous materials, the concluding Section 6.4 is devoted to first results concerning the occurrence of diffusion hysteresis in hierarchical pore systems.

6.1 Diffusion in compacted nanoporous material

Fig. 13 displays the effective diffusivity of cyclohexane in compacted MCM-41 agglomerates at room temperature. The agglomerates are small beads with diameters of the order of hundreds of micrometers which exhibit a most complex “hierarchical” structure. Their basic units are mesoporous quasi-crystallites of MCM-41 structure type with a few tens of nanometers in diameter which, in turn, form clusters or grains with dimensions of a few hundred nanometers. These grains become visible in the electron microscopy image in the inset of Fig. 13 and are, finally, compacted to the investigated beads. Thus, in addition to the genuine mesoporous space in the interior of the MCM-41 crystals, the beads under study contain two more types of pores, namely, in the space between the quasi-crystals and, larger ones, between the grains. Most remarkably, the free space between these grains, in conjunction with a small fraction of larger transport pores traversing the beads, has been identified to be essentially exclusively relevant for mass transfer within these beads and, hence, for any transport-related feature during the technological application of these materials. Note that, being able to cover molecular displacements much smaller than the bead diameters but much larger than the intraparticle structural correlation lengths determined by the diameters of the quasi-crystalline domains and their agglomerations to the grains appearing in the inset of Fig. 13, PFG NMR is ideally suited for this type of measurements.

Following the procedure described in Sections 5.1 and 5.2, which we have referred to, already, at the beginning of this review, in ref. 139 the analytic expression of the effective diffusivity (which, for this particular case, is given by eqn (29)) is derived in the form

\[
D_{\text{eff}} \approx (1 - \frac{1}{9}) \frac{\rho_s \varphi \lambda^2}{\rho_s \eta \theta d_M + \lambda}
\]

where, as used already in eqn (22), \(\varphi\) stands for the average molecular velocity, \(\rho_s\) and \(\rho_l\) denote the guest densities in the gaseous and liquid phases, \(\eta\) denotes the ratio between the genuine mesopore volume of the MCM-41 structure and the volume of the macropores relevant for mass transfer and \(\lambda\) denotes the ratio between the volume of the large transport pores and the total macropore volume (characterized by the mean pore size \(d_M\)). \(\lambda\) is the molecular free path length in the bulk gas phase, and \(\theta\) is the mesopore filling. Note that the relative pressure was kept small enough so that capillary condensation in the transport (macro-) pores could be excluded.

It is remarkable that, by using eqn (30), it has been possible to nicely reproduce the rather complex dependence of the intra-bead diffusivities on the externally applied guest pressure (full and dotted lines in Fig. 13) with the use of only two fitting parameters, namely with \(x = 0.16\) and \(d_M = 0.61\) μm where, moreover, both quantities are seen to be in the range of the expected magnitudes. On following the variation of the diffusivity with decreasing pressure, with eqn (30) the steep increase at a relative pressure \(z \approx 0.3\) may be easily associated with the evaporation of the fluid out of the mesopores, leading to a dramatic decrease in the filling of the mesopores (\(\theta\)) corresponding to an increase in the relative amount of molecules in the transport pores \(p_{\text{mes}}\) in eqn (29)).

Note that the diffusivities are in no way affected by the diffusivities within the micro-crystalline compartments of genuine MCM-41 pore structure. On the contrary, by following the long-range diffusion in such beads, e.g. by macroscopic measuring techniques like uptake and release experiments, no information about diffusion in the genuine MCM-41 structure are possible. In fact, this type of experiments requires the application of macroscopically ordered particles, ideally single crystals. These confinements do exist quite generally for diffusion studies with compacted particles consisting of nanoporous constituents. FCC catalysts are an important representative of such systems. The same situation as just illustrated for compacted MCM-41 has been demonstrated to also exist for long-chain n-alkanes in FCC catalyst particles.

![Fig. 13](image-url)
where the overall diffusivities were shown to be exclusively determined by the rate of long-range diffusion, without any notable impact of the intracrystalline diffusion on the zeolitic components.147–149

6.2 Diffusion in a continuous space of nanopores with larger pores embedded

Owing to their regularity, ordered hierarchical porous materials offer particularly convenient conditions for an in-depth study of structure–mobility correlations. We are going to base, therefore, our considerations on diffusion studies on such a material (ordered silica “PIB-IL”), consisting of a regular array of spherical pores with diameters of about 20 nm, connected by worm-like cylindrical mesopores with diameters of 2–3 nm. Fig. 14 shows a TEM image of the material.

A summary of the sorption and diffusion data obtained, at room temperature, with cyclohexane as a guest molecule in this material is provided by Fig. 15. After filling of the continuous bulk phase of nanopores at a relative pressure of about 0.3, filling of the cavities is seen to give rise to a pronounced hysteresis where the high diffusivities on the adsorption branch are easily understood to result in consequence of the free space in the cavities. Note the (slight) decrease in loading with decreasing pressure in the desorption branch following full saturation. In Section 5.3 we have already referred to this effect as an indication of fluid stretching, accompanied with an increase in the diffusivities.

Before continuing our discussion of the guest diffusivities we consider, in some more detail, the possible patterns of the guest trajectories. Two special cases are shown in Fig. 16. Inside the nanoporous bulk phase of the material, the trajectories exhibit a random diffusion path typical of Brownian motion while the dispersed, large mesopores are traversed via Knudsen flights, given the fact that, in the considered pressure range, mutual collisions of the molecules within these pores may be excluded. As the main difference between the cases considered, free flights through the large cavities in Fig. 16a are followed by many more in one and the same cage while the guest molecule in Fig. 16b is seen to pass a given large cavity only once. In detailed dynamic Monte Carlo simulations in ref. 129, this difference is referred to differences in the probability of molecular transitions from the nanoporous bulk phase into the gas phase of the mesopores which in Fig. 16a is considered to be much larger than in Fig. 16b.

Following the procedure applied with eqn (20) and (21) for displacements along the mesopore surface and through the gas phase, we are going to consider the sequence of displacements in only the nanoporous continuum and in the dispersed cavities. Fig. 17 shows the sequence of such displacements in the latter case, again considering the two cases of high (a) and low (b) transition probability from the nanoporous bulk phase into the cavities.

In the case considered in Fig. 16b and 17b (realized with sufficiently low escape rates from the nanoporous continuum into the cavities), the individual displacements are easily seen to give rise to a sequence of elementary steps independent from each other. This is the prerequisite for normal, unrestricted diffusion. Hence, the contribution of guest propagation through the cavities to overall diffusion follows in exactly the same way as eqn (21) and (22), where the numerical pre-factor

Fig. 14 TEM image of ordered porous silica (PIB-IL). The white spots are associated with spherical voids in periodic arrangement, embedded in a bulk phase traversed by a network of (notably smaller) mesopores.129

Fig. 15 Effective diffusivities (top part, filled symbols) and relative amounts adsorbed (lower part, open symbols) of cyclohexane in PIB-IL at room temperature measured during adsorption (filled and open circles) and desorption (filled and open rectangles).129

Fig. 16 Schematic representation of trajectories of guest molecules in porous silica PIB-IL (see Fig. 14) with cavities (white circles, gas phase) embedded in a nanoporous bulk phase (in blue, saturated), considering the cases of high (a) and low (b) transition probability from the nanoporous bulk phase into the cavities.129
in eqn (22) is now found to be $1/8$ rather than $1/3$, with $d$ denoting now the cavity diameter.

Adopting the simulations to the micro-dynamic situation given at full saturation of the nanoporous bulk phase with still a free gas phase in the cavities, with cyclohexane as a guest molecule, the escape probability from the nanoporous continuum into the cavity gas phase can be demonstrated to be in fact small enough so that it is justified to assume the situation shown in Fig. 16b and 17b. This means, in particular, that the overall diffusivity can be determined in complete analogy with eqn (18) and (23), i.e. by implying the validity of the fast-exchange relation. Fig. 18 demonstrates that the theoretical estimate of the diffusivities based on these relations and the relative population of the cavities directly resulting from the adsorption isotherm (Fig. 15) nicely reproduces the experimentally observed behavior.

With both the experimental data and the theoretical analysis, the presence of the cavities is shown to lead to an enhancement of the guest diffusivity. The observed diffusivities attain a maximum (at intermediate pore filling, as observed already with purely mesoporous material, e.g. in Fig. 5 and 9) which exceeds the diffusivity in the pure nanoporous bulk phase by a factor of about 1.5. Such a – modest – enhancement is not unexpected since the existence of fast migration paths (Knudsen flights through the gas phase) is easily understood to accelerate the overall mass transfer. However, one has to be aware of the fact that the range allowing this fast transport does not form a continuous network traversing the whole material. Instead, any trajectory through the material has to involve passages through the bulk which ensure that, irrespective of further increasing transfer rates through the cavities, the overall diffusivity remains limited. Exactly this situation is shown in Fig. 16a and 17a: here, an increasing contribution of mass transfer through the cavities (appearing in an increasing number of flights) is seen to lead to an increasing anti-correlation in the displacements, resulting in an overall displacement (Fig. 17a) which is more and more retarded in comparison with a sequence of uncorrelated displacements (Fig. 17b). Such a situation is not compatible anymore with the fast exchange relations (eqn (18) and (23)) which imply that, by enhancement of the diffusivity in any of the involved regions, also the overall (effective) diffusivity could be enhanced unlimitedly.

The occurrence of dispersed mesopores, separated from each other, is also known from de-aluminated zeolite Y, the main active component in FCC catalysts. The de-alumination procedure during their fabrication gives rise to the formation of isolated cavities. While, on the basis of a formal application of the fast exchange model, under reaction conditions a dramatic increase in the guest diffusivities might be expected, PFG NMR measurements of the intracrystalline diffusion did not reveal any significant difference between the diffusivities in the starting material and in the de-aluminated zeolite – in complete agreement with our expectation that the rate of mass transfer can only moderately be enhanced by the inclusion of high-diffusivity regions, separated from each other: Significant transport enhancement is only possible with a network of diffusion “highways” traversing the nanoporous bulk phase.

In conclusion, we refer to a most helpful option of correlating the overall diffusivity in complex systems with the individual constituents of mass transfer, suggested by the formal equivalence
of Fick’s and Ohm’s laws. The fast exchange model of diffusion leading to eqn (18) and (23) is easily recognized to correspond to a parallel connection of electrical conductors: In both cases, infinity in the conductivity (diffusivity) of one branch leads to overall infinite conductivity (diffusivity). Diffusion through regions of alternating diffusivity, however, has its analogue in the series connection of electrical conductors, where the overall conductivity (diffusivity) remains limited as long as the conductivity (diffusivity) in one of these sub-regions remains limited. This intuitively anticipated behavior has been found to be nicely reflected by the diffusivity data presented in this section where the presence of the large pores, separated from each other, is shown to give rise to an only moderate enhancement of the overall diffusivity. In the subsequent section, dedicated to mass transfer in hierarchical materials with mutually interpenetrating pore systems, we shall see that this limitation may be easily overcome. Moreover, the series-parallel approach for diffusion in complex media will again prove to serve as a helpful means for rationalizing the overall diffusion patterns.

6.3 Diffusion in bi-continuous pore spaces

We consider, as a model system, three different specimens of calcium-exchanged zeolite LTA, one purely microporous (NaCaA-0) and two microporous ones with mesopores traversing the whole crystal body, with total volumes of 0.110 cm$^3$ g$^{-1}$ (NaCaA-2) and 0.218 cm$^3$ g$^{-1}$ (NaCaA-5), respectively. The size of the mesopores is about 5 nm. Fig. 19 shows representative SEM images of the samples.

Fig. 20 shows an Arrhenius plot of the diffusivity data obtained with these samples, using ethane as a guest molecule. The PFG NMR measurements were performed with fused sample tubes and with a loading corresponding to three molecules per micropore. Two samples, also loaded with ethane, where the mesopores were saturated with deuterated cyclohexane, were additionally prepared. The cyclohexane molecules are too bulky for entering the genuine LTA micropore space and, by applying deuterated species, any disturbance by interference with the $^1$H)PFG NMR signal of the probe molecules (ethane) was avoided.

The diffusivities in the purely microporous specimen are connected by a straight line resulting as the best fit to an Arrhenius dependence. A parallel shift of this line to lower values nicely approaches the ethane diffusivities with blocked mesopores. This is exactly the behavior expected by following eqn (19), now with $D$ denoting the diffusivity in the genuine micropore space of LTA and with a tortuosity $\tau$ emerging in consequence of the detours in the ethane diffusion paths caused by the blockage of the mesopores.

Since both pore spaces penetrate each other, following the reasoning of Sections 5.1 and 6.2, the overall diffusivity may be represented in the form

$$D_{\text{intra}} = D_{\text{micro}} + p_{\text{meso}} D_{\text{meso}}$$

(31)

with $p_{\text{micro(meso)}}$ and $D_{\text{micro(meso)}}$ denoting, respectively, the relative amounts and the diffusivities of the guest molecules in the micro- (meso-) pore spaces. It has been demonstrated already in Section 5.1 that, irrespective of the dramatic difference in the population in the two regions [$p_{\text{meso}} \ll p_{\text{micro}} \approx 1$], the second term in eqn (31) may lead to a significant enhancement in the overall diffusivity, as an immediate consequence of the large mean free paths in the void space of the mesopores, giving rise to Knudsen-type molecular propagation. In fact, using propane (with a particularly small diffusivity in the LTA micropores) the diffusivity in mesoporous zeolite LTA was shown to exceed the micropore diffusivities by several orders of magnitude.
This option does not exist as soon as mass transfer in the mesopores is impeded by the existence of a liquid phase: The diffusivity of the ethane molecules in the mesoporous space is now slowed down dramatically. This is a consequence of the dramatic decrease of \( D_{\text{meso}} \), which now refers to the diffusivity of ethane, if dissolved in cyclohexane, rather than to the ethane diffusivity in the free pore space. Rather than accelerating intracrystalline mass transfer, the presence of mesopores is thus giving rise to its decrease by a tortuosity factor \( \tau \). The tortuosity is known to increase, in general, with increasing volume fractions of the forbidden regions \(^7,^{150,153,154} \) so that it is not unexpected that the ethane diffusivities in the samples with a larger fraction of blocked mesopores are distinctly below those with the smaller content of mesopores.

As a consequence of confinement to the closed volume of the PFG NMR sample tubes (see the last paragraph of Section 4.2), the ethane pressure within the sample and, hence, the relative amount \( p_{\text{meso}} \) of ethane in the mesopores increases with increasing pressure, following the Arrhenius dependence

\[
p_{\text{meso}} \propto \exp\left( -\frac{E_{\text{ads}}}{RT} \right)
\]  

with \( E_{\text{ads}} \) denoting the isosteric heat of adsorption.\(^7,^{152} \) This dependence is indicated by the broken line in Fig. 20. Its slope is given by the value \( E_{\text{ads}} = 28 \, \text{kJ mol}^{-1} \) as taken from ref. 156. It, simultaneously, indicates the contribution of the second term in eqn (31) to the overall intracrystalline diffusivity with varying temperature since \( D_{\text{meso}} \) does only vary with the square root of the temperature and, hence, remains essentially constant in the considered temperature range. Nicely reflecting the exponential increase of this contribution with increasing temperatures, for high temperatures the slope of the Arrhenius plots of the ethane diffusivities in the unblocked mesoporous zeolites is seen to approach that of the broken line while, in the limit of sufficiently low temperatures, the diffusivities in the zeolites with unblocked mesopores approach those in the zeolites with blocked mesopores.

For a complete understanding of the temperature dependence of the ethane diffusivities in mesoporous zeolite LTA we have to refer to the considerations of the previous section, notably to Fig. 16 and 17. With decreasing temperature, on encountering the surface to the mesopores more and more guest molecules in the mesoporous bulk phase will be unable to escape into the free space. This is an immediate consequence of the decrease in thermal energy which as well appears in the decreasing equilibrium pressure in the surrounding atmosphere. Molecular displacements in the micropores towards the surface, notably towards the internal one formed by the mesopores, will thus be followed predominantly by displacements back into the range of the micropores. Hence, on considering micropore diffusion, we are confronted with exactly the situation discussed in the context of Fig. 16 and 17 for diffusion in the free space. Anti-correlations in guest displacements close to the interface with the mesopores do thus lead to a reduction in the diffusivities in comparison with the purely microporous zeolites. This effect loses its relevance with increasing temperature. The experimentally observed steep increase in the ethane diffusivities in NaCaA-2 and -5 with increasing temperature (Fig. 20) must therefore be attributed to an increase in both the fraction of molecules contributing of mesopore diffusion and in the effective diffusivities of mass transfer in the space of the micropores due to diminishing anti-correlations in the molecular displacements.

In a semi-quantitative way the effect of anti-correlations in molecular displacements can be reflected by the series-parallel formulae of diffusion in heterogeneous media as discussed at the end of Section 6.2. Using the notation

\[
D_{\text{intra}} = p_1 D_{\text{micro}} + p_2 p_{\text{meso}} D_{\text{meso}} + p_3 \left( \frac{D_{\text{micro}} p_{\text{meso}} D_{\text{meso}}}{D_{\text{micro}} + p_{\text{meso}} D_{\text{meso}}} \right) \tag{33}
\]

we take into account that, in the hierarchical pore space considered, there are essentially three different types of diffusion paths, namely paths exclusively within the spaces of either the micropore- or the mesopores (first two terms) or paths through both spaces where the mesopores may be imagined as “interruptions” in a continuous space of micropores (third term). Since the heat of adsorption notably exceeds all other activation energies, the temperature dependence of eqn (33) is determined by that of \( p_{\text{meso}} \). With eqn (33), one may thus consider two limiting cases. For high temperatures \( (p_{\text{meso}} D_{\text{meso}} \gg D_{\text{micro}}) \) as a consequence of the increase of \( p_{\text{meso}} \) with increasing temperature,

\[
D_{\text{intra}} \approx p_2 p_{\text{meso}} D_{\text{meso}} \quad (p_1 + p_3)D_{\text{micro}} \tag{34}
\]

The other limit refers to low temperatures \( (p_{\text{meso}} D_{\text{meso}} \ll D_{\text{micro}}) \)

\[
D_{\text{intra}} \approx p_1 D_{\text{micro}} + (p_2 + p_3) p_{\text{meso}} D_{\text{meso}}. \tag{35}
\]

With these two equations, the ethane diffusivities in the mesoporous zeolites (with the mesopores left unblocked) can be nicely rationalized and referred to our model considerations: Even at the highest temperatures considered in this study, the values of \( D_{\text{intra}} \) are still of the order of \( D_{\text{micro}} \). It is hence in complete agreement with our expectation that the slope in the Arrhenius plot of the effective diffusivity of ethane in NaCaA-5 as shown in Fig. 20 is intermediate between those of \( D_{\text{micro}} \) (broken line) and \( D_{\text{meso}} \) (full lines). With eqn (35) we note that, with decreasing temperature and, thus, with decreasing values of \( p_{\text{meso}} \) and, hence, of \( p_{\text{meso}} D_{\text{meso}} \), \( D_{\text{intra}} \) drops to \( D_{\text{micro}}/\tau \), i.e. to the level of micropore diffusion, impeded by the presence of the, then essentially inaccessible, mesopores. In this range, the decay of \( D_{\text{intra}} \) is seen to nicely follow that of \( p_{\text{meso}} \) as expected.

Fig. 21 provides a summarizing representation of the diffusivities in either of the two pore spaces, if mass transfer through the other one is totally excluded. In the left, lower part, represented by triangles, we identify the diffusivities of ethane in the micropores, namely in the purely microporous specimens and in the mesoporous zeolites where, in comparison with diffusion in the micropores, mass transfer in the mesopores is essentially inhibited. These data are taken from Fig. 20. The diffusivity data (represented by circles) in the upper right part of the representation refer to cyclohexane which, as a consequence of its larger molecular size, can only be
accommodated by the mesopores. These data have been determined by PFG NMR measurement of an additional set of samples where the mesopores are saturated with cyclohexane (this time, for the performance of $^1$H PFG NMR, clearly, in the proton-containing, normal form). At the very right, for comparison, also diffusivity of cyclohexane in the neat liquid is given. The data points nicely reflect the expected tendency that the diffusivity in a given subspace decreases with the decrease of its volume fraction. Thus, the micropore diffusivity (as probed with ethane) in NaCaA-2 is found to be larger than in NaCaA-5, while exactly the opposite is true with the mesopore diffusivities as probed with cyclohexane.

The information provided by the absolute values of the tortuosities determined for the ethane diffusivities in the mesoporous specimens of LTA may be further exploited by reference to the results of model calculations for the tortuosities in certain geometries. For a medium with parallel, regularly arranged impermeable cylinders for displacements perpendicular to the cylinder axes, e.g., it holds

$$\tau = \frac{1 + \phi}{1 - \phi}$$

(36)

where $\phi$ denotes the volume fraction of the obstacles. Assuming a mass density of about 2 g cm$^{-3}$ for the purely microporous zeolite NaCaA, the volume fractions of the mesopores in NaCaA-2 and -5 result to be $\phi = 0.18$ and 0.30, respectively. With these numbers, with eqn (36) the diffusivity must be expected to be reduced by about 30% in NaCaA-2 and 50% in NaCaA-5, in striking contrast with the experimentally observed decrease of as much as one order of magnitude. Instead of being extended in channel-like form, the mesopores should therefore be expected to be arranged in a way by which, after being converted into regions of extremely low diffusivity and/or permeability, and, hence, being essentially blocked, they give rise to a much more pronounced reduction in the diffusivities. Such a situation would result for mesopores with plate-like extensions which, following the SEM images shown in Fig. 19, can in fact be expected to be formed predominantly in parallel with the 100, 010 and 001 planes. The parallel arrangement of diffusion inhibitors is an approved technology in the fabrication of polymer packing foils where the incorporation of aligned flakes is known to lead to significantly reduced permeation rates.$^{157}$

### 6.4 Diffusion hysteresis in hierarchical materials

The detection of diffusion hysteresis in mesoporous materials as reported in Section 5.3 provided us with a new tool for the exploration of pore space architecture, whose potentials are a topic of current exploration. With the present section we are going to illustrate how, with the increasing complexity of the pore space in hierarchical materials, also the hysteresis patterns become more complex, offering a most attractive and promising field of future research.

As an example, we consider the uptake and release of cyclohexane in a hierarchical activated carbon (referred to as MA2$^{158}$). The almost spherical particles (spheres with diameters of about 0.15–0.50 mm) consist of mutually interpenetrating networks of micropores and mesopores with essentially equal total volumes and mean sizes of about 1 and 20 nm, respectively. Again, with diffusion path lengths notably smaller than the particle diameters and much larger than the pore diameters, PFG NMR is ideally suited for tracing intra-particle diffusion. Fig. 22 shows, in a joint representation with the total amount adsorbed (bottom), the thus-determined effective diffusivities of cyclohexane at room temperature (top) as a function of the external pressure. The representation, essentially, comprises the pressure range where the micropores are already saturated and pressure steps do only affect the loading of the mesopores. During adsorption, these steps are observed to lead to only

![Fig. 21](image1.jpg)

**Fig. 21** Comparison of the diffusivity in the space of micropores (probed with ethane; triangles) and mesopores (cyclohexane; circles) of the mesoporous zeolite NaCaA at room temperature. Given, for comparison, are also the diffusivities of ethane in the purely microporous zeolite and of cyclohexane in the neat liquid. The lines are shown to guide the eye.$^{155}$

![Fig. 22](image2.jpg)

**Fig. 22** (a) Diffusivities of cyclohexane at 298 K in hierarchical activated carbon (referred to as MA2$^{158}$). The almost spherical particles (spheres with diameters of about 0.15–0.50 mm) consist of mutually interpenetrating networks of micropores and mesopores with essentially equal total volumes and mean sizes of about 1 and 20 nm, respectively. Again, with diffusion path lengths notably smaller than the particle diameters and much larger than the pore diameters, PFG NMR is ideally suited for tracing intra-particle diffusion. Fig. 22 shows, in a joint representation with the total amount adsorbed (bottom), the thus-determined effective diffusivities of cyclohexane at room temperature (top) as a function of the external pressure. The representation, essentially, comprises the pressure range where the micropores are already saturated and pressure steps do only affect the loading of the mesopores. During adsorption, these steps are observed to lead to only
slight changes in loading so that, on the basis of the observation with purely mesoporous materials (Section 5.3), equilibration must be expected to require rather long time spans. Pressure steps during desorption are generally followed by much more pronounced changes in loading though, clearly, also in this case it is not clear how long establishment of (quasi-)equilibrium would take. Due to limitation in the total measuring time, only in some special cases (Fig. 22b and d) equilibration times over several hours were followed while otherwise, for all loadings shown in Fig. 22c, the measurements were uniformly performed 10 minutes after the pressure step, followed by the PFG NMR diffusion measurements (Fig. 22a).

In addition to the experimental data, Fig. 22a also show an estimate of the diffusivities following from eqn (31) with the simplifying assumption that, in addition to micropore diffusion, only mass transfer through the free space of the mesopores (i.e. Knudsen diffusion, eqn (22)) contributes to the overall diffusivity. Since the relative amount \( p_{\text{meso}} \) of molecules contributing to this mode of transportation is very small and, hence, \( p_{\text{meso}} \propto P \), disregarding any significant reduction of the mesopore free volume, \( \text{via eqn } (31) \) the linear increase of the overall diffusivity with increasing pressure as indicated by the broken line becomes immediately understandable. For ensuring that the estimate leads to exactly this value where the diffusivities on the adsorption and desorption branches coincide, a tortuosity factor of \( \tau = 1.3 \) has to be assumed. Given the rather rough model, this value is clearly found to be within a reasonable order of magnitude.

The feasibility of this simple model may be further supported by a closer inspection of the value of the overall diffusivity attained after 20 h (Fig. 22b). Now we imply that the overall diffusivity results as a superposition of the diffusivities in the micro- and mesopores. Correspondingly, we start our consideration with eqn (18), where \( i \) refers to the micro- and mesoporous spaces. With the relative amounts \( p_i \) of molecules as resulting from the two pore space volumes and taking the diffusivity at the low-pressure end as the micropore diffusivity, the cyclohexane diffusivity in the mesopores may be determined as \( 6.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \). Comparison with the diffusivity of cyclohexane in the free bulk \( (1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}) \)\(^{39} \) yields a tortuosity factor of the order of 2 for diffusion in the mesopores which is, once again, found to be of a reasonable order of magnitude.

We note that the overall diffusivities measured during molecular uptake are below and during release above the theoretical estimates. This outcome seems to suggest that, further approaching each other, the diffusivities on the two branches might, eventually, approach the theoretical estimates. Definite answers, however, would require much more detailed experiments in the future.

7 Concluding remarks and perspective

The advent of an impressive multitude of new mesoporous materials, promoted by technological requirement, and the fascinating prospects of their exploitation as tailored host materials for fundamental research, is accompanied by a corresponding multitude of new questions concerning guest dynamics. While it took quite a while before the surprises, emerging with the application of microscopic diffusion measurements to mass transfer in purely microporous materials, initiated a paradigm shift in our understanding of intracrystalline diffusion, the particular challenges of diffusion studies with mesoporous materials – and, among them, in particular, with those of hierarchical pore structure – are immediately apparent, given the complex structure of such systems which is easily seen to need a whole set of parameters for an adequate description of their internal dynamics. The “history dependence” of the guest distribution in such host–guest systems, which gives rise to the well-known effect of sorption hysteresis and which also affects intrinsic molecular dynamics, additionally complicates the situation.

Based on first experimental studies, we have tried to highlight the potentials for the exploration of these questions, provided by the pulsed field gradient (PFG) NMR technique. Combining the option of measuring both the concentrations of the guest molecules and their diffusivities, PFG NMR has proven to be a particularly powerful and versatile technique for diffusion measurement in such systems. It is important to emphasize that, on considering mass transfer in purely microporous materials, the evidence of PFG NMR about the rate of intracrystalline diffusion found notable support by the evidence of molecular dynamic simulations and of measurements by quasi-elastic neutron scattering. The spectrum of quite different mechanisms which may become rate controlling for overall mass transfer in the, in general, much more complex pore space of mesoporous and, notably, of hierarchical materials necessitates a completion of the tool set complementing the experimental evidence as provided by PFG NMR. In this context, the novel options of single-particle fluorescence imaging\(^{160–162} \) and high-resolution microscopy\(^{163} \) ensuring the in situ characterization of solid catalysts and nanoporous adsorbents over essentially all length scales\(^{160,164–167} \) are of particular relevance.

In parallel with the experimental evidence provided by direct measurement, an in-depth understanding of mass transfer phenomena in complex mesoporous materials notably benefits from the performance of simulations correlating the structural features resulting from such studies with their consequences on molecular diffusion.\(^{168–170} \) By analyzing the correlation between subsequent displacements, we have employed this access (notably the options of dynamic Monte Carlo simulations) for demonstrating that in hierarchical materials with smaller and larger mesopores overall fluid diffusivities are promoted by the presence of the larger mesopores depending, essentially, only on their volume fraction rather than on their topology. In such cases, however, the gain in mobility by the presence of the larger mesopores remains rather limited, quite in general.

The situation is notably changed, however, when the diffusivity in the continuous pore space is dramatically slowed down as, e.g., in the micropores of a zeolitic bulk phase. In this case
(as demonstrated with mesoporous zeolite NaCaA), the incorporation of a network of mesopores may lead to an enhancement of intracrystalline diffusion over orders of magnitude while, for dispersed mesopores, separated from each other, again only a rather modest mobility increase might be attained. It is also shown that transport enhancement through networks of mesopores is clearly only possible if they are accessible for mass transfer. If this is not the case, the presence of the mesopores would even lead to a notable decrease in the intracrystalline diffusivities. Hence, with increasing time on stream, the technological benefit of nanoporous materials with hierarchical pore spaces in comparison with their purely microporous equivalent might even be converted into its opposite when, e.g., by coke deposition on the internal surface of the mesopores, molecular exchange with the microporous space is excluded and the mesopores act as resistances rather than as highways for molecular transport.

The exploration of guest diffusion in mesoporous material, notably with hierarchical pore systems, is only in a very initial stage. As a microscopic technique, PFG NMR offers particularly promising potentials for elucidating the various features of mass transfer in such systems. The examples given in this review address, simultaneously, the more general issue to recognize mass transfer as a crucial phenomenon deciding about the performance of technologies operating with such systems and their optimization. An in-depth study of the physics behind these processes is doubtlessly among the key prerequisites for such efforts. The exploration of the rather complex interrelation between phase changes (including those into and out of the supercritical state) and molecular mobilities, as one of the main topics of this review, has all potentials for opening completely novel routes towards transport-optimized technologies.

With the advent of metal–organic frameworks (MOFs) and the option to synthesize “breathing” host materials, 171–177 molecular mobilities may now also be “triggered” by transitions in the host lattice. Just as phase transitions in the guest phase considered in this review, also changes in the host structure may be purposefully induced by appropriately chosen variations in pressure and/or temperature. Such lattice transitions may even be induced externally, e.g. by irradiation at a suitably chosen frequency. 178,179 Further challenges opening up in the exploration of mass transfer phenomena with nanoporous materials include the investigation and application of hierarchically organized nanoparticles in separation and heterogeneous catalysis 180–183 and of host materials with chiral pore structure for enantioselective catalysis and separation. 184,185

The field of problems related to mass transfer in nanoporous materials is thus seen to be essentially unlimitedly extended, just like the nature of the host materials themselves is of essentially unlimited diversity. Though macroscopic measurement of the rate of exchange between these systems and the surrounding is a very important first step for assessing the role of mass transfer quite in general, detailed information about the actual processes contributing to the overall phenomenon necessitates the in-depth investigation by more sophisticated techniques. Being able to record molecular propagations over microscopic distances, PFG NMR has proved to be a most useful technique for attaining this type of information. The examples given in this review have been selected for illustrating these potentials. Further progress will decisively depend on the successful incorporation of these potentials in the spectrum of information provided by the whole tool box of characterization techniques for such systems and by the various techniques of molecular modeling. We would be happy if our contribution to this issue, dedicated to mesoporous materials quite in general, might contribute to this development.

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