Diffusion in nanopores: correlating experimental findings with “first-principles” predictions

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Abstract

Measurement of molecular diffusion in nanoporous host materials, which are typically inhomogeneous and anisotropic, often involves an intricate web of factors and relations to be taken into account since the associated diffusivities are a function of the diffusion path of the guest molecules during a given observation time. Depending on the observation time, therefore, the result of the experimental measurement can point to completely different conclusions about the underlying diffusion phenomena. The risk of misinterpretation of the experimental data, by correlating them with irrelevant phenomena, may be reduced if there is an option to compare the data with the results of totally independent measurements. The present communication addresses this issue with reference to the particular potentials of pulsed field gradient NMR and microimaging by infrared microscopy as techniques of microscopic diffusion measurement.

Keywords Molecular diffusion · Nanoporous material · PFG NMR · Tracer desorption · Infrared microscopy · Microimaging

1 Introduction

Diffusion, i.e. random movement of the elementary constituents of matter, is an omnipresent phenomenon in nature and in the very heart of many processes. This includes, in particular, matter upgrading by molecular separation and catalytic conversion in nanoporous solids. The gain in value-added products can, obviously, never be faster than the rate of transportation of the involved elements. Measurement of molecular diffusion in nanoporous materials is therefore an important task with reference to both fundamental research and technological application. Different from bulk materials as solids, liquids and gases (Jost 1960; Kizilyalli et al. 1999) where diffusion is exclusively a function of the diffusants, i.e. of the atoms or molecules and their “arrangement”, the diffusion in nanoporous material depends on both the host and the “guests”. Since nanoporous host materials are not available, as a rule, as homogeneous, quasi-infinitely extended entities, the measurement of guest diffusion is often additionally complicated by the fact that

the associated diffusivities may become a function of the displacements over which, in a given experimental setup, the diffusion paths of the molecules are recorded. Further difficulties arose with the advent of hierarchically organized materials (Groen et al. 2007; Mehlhorn et al. 2012; Möller and Bein 2013; García-Martínez and Li 2015; Valtchev and Mintova 2016; Galarneau et al. 2016; Hartmann et al. 2016; Chen and Snurr 2020), necessitating the development of multiscale approaches for transport simulation combining interfacial phenomena, like adsorption and partitioning, with mass transfer (Tallarek et al. 2019).

It has therefore become common practice (Kärger et al. 2012; Kärger and Ruthven 2016) to distinguish between microscopic and macroscopic techniques of diffusion measurement. In macroscopic measurements, diffusion path lengths exceed the size of the individual nanoporous particles/crystallites, but one strives to assure that the overall behavior is still controlled by intracrystalline/intraparticle diffusion—or that, at least, overall mass transfer allows its determination (Ruthven and Brandani 1997; Ruthven et al. 2008). In microscopic diffusion measurement, the diffusion path lengths considered in the experiments are shorter than or of the order of the crystal/particle extensions.

The development of both types of measurements along with meaningful comparisons has been substantially

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beneficial (Brandani and Ruthven 2000; Kärger 2003). Comparative studies gave, *inter alia*, rise to the detection of a series of side effects like lattice degradation (Ruthven 2012) and formation of additional transport resistances either in the intracrystalline space (Vasenkov and Kärger 2002; Feldhoff et al. 2009; Guo et al. 2019) or on the external surface (Heinke et al. 2007; Kärger 2014b; Remi et al. 2015; Rao et al. 2017). If they are not properly taken into account, the measurements can give rise to completely wrong conclusions about the underlying diffusion phenomena. Their detection has remained a challenging task until today, notably on considering heterogeneous systems like mixed matrix membranes (Mueller et al. 2015; Friebe et al. 2017; Dutta and Bhatia 2018; Hwang et al. 2018; Forman et al. 2019).

Experimental measurement is, as a rule, subject to at least two sources of uncertainty. One is related to the fact that there is always a limit in the attainable accuracy. Such uncertainties are typically marginal – only a few percent. The other, much more serious source of errors is related to the possibility that the quantity accessible by experimental measurement does not match the quantity one is finally interested in. In such cases it may happen that, irrespective of primary measurement data of highest accuracy, the quantities of interest, determined from these data, are completely wrong. This occurs if data analysis is based on wrong suppositions.

As a “classical” example, one may refer, in this context, to diffusion measurement in nanoporous materials by recording of molecular uptake and release. If, due to the existence of substantial transport resistances in the external particle/crystal surface, uptake and release are controlled by the permeation through this “surface barrier” rather than by intracrystalline/intraparticle diffusion, then the data analysis based on diffusion limitation give rise to “diffusivities”, which have nothing to do with the genuine intracrystalline/intraparticle diffusivities. They could be possibly used to estimate a lower limit of this value, by correlating the time constants of the two limiting cases (Kärger and Ruthven 2016). A distinction between the two limiting cases based on the differences in their time dependencies may get increasingly complicated due to variation in surface permeabilities within a single batch of particles/crystals (Remi et al. 2015). There are, however, good prospects to achieve such a distinction in “partial loading” experiments (Brandani et al. 1995; Gunadi and Brandani 2006; Chmelik et al. 2009) by considering sequences of uptake and release with separations smaller than the uptake and release times. While, in such experiments, relative uptake and release is found to be accelerated under diffusion limitation, this effect is progressively reduced with increasing influence of surface resistances.

The risk of misinterpretation of the primary data of experimental measurements by associating them with phenomena to which they are not related—for example, the (unjustified)

correlation of molecular uptake and release with intracrystalline diffusion, in the case of barrier limitation—may be reduced if there is an option to compare the data with the results of a totally independent measurement. In this context, we are going to consider the possibility of correlating the message of microscopic diffusion measurement with the evidence provided by other, independent measuring techniques. We are, in particular, asking up to which extent it is possible to predict certain features of these measurements on the basis of well-established (“first-principles”) knowledge of the systems under study. We shall refer to measurements by both pulsed field gradient (PFG) NMR (Sect. 2) and Micro-imaging (Sect. 3).

2 Pulsed field gradient NMR

2.1 Measuring principle

Diffusion measurement by pulsed field gradient (PFG) NMR (Slichter 1980; Kimmich 1997; Stallmach and Kärger 1999; Price 2009; Valiullin 2016) may be rationalized on the basis of the quasi-classical conception of NMR, implying that the nuclear spins under consideration (in general protons, the nuclei of hydrogen) combine the properties of both a rotating gyroscope and a magnetic dipole. The individual spins rotate, therefore, within a magnetic field around its direction at an angular frequency, proportional to the intensity of the magnetic field. This rotating magnetization induces a voltage in the NMR sample coil, which is recorded as the NMR signal. PFG NMR is based on the application of two “field gradient pulses”, i.e. two small intervals of time during which the constant magnetic field is superimposed by two highly inhomogeneous fields. They are arranged in such a way that the second pulse compensates the defocusing generated by the first one. This, however, is only completely fulfilled if each individual spin has “seen”, at the instants of the two field gradient pulses, the same magnetic field. Any shift of a molecule (and, hence, of a nuclear spin within this molecule) in gradient direction during the time interval between the two field gradient pulses, however, gives rise to incomplete refocusing. This spin does, therefore, contribute with only the cosine of its phase difference to the direction of overall nuclear magnetization to the NMR signal. From this consideration one may immediately note for the attenuation of the signal due to diffusion in PFG NMR experiments

$$S(m, t) = S(0, t) \int_{-\infty}^{\infty} \cos(mz) P(z, t) dz \quad (1)$$

where m is a measure of the intensity of the field gradient pulses. Their mutual separation t appears as the observation time in PFG NMR diffusion studies. For simplicity it is

implied to be much larger than the duration (the “width”) of the field gradient pulses. $S(0, t)$ is the intensity of the signal without field gradients applied. $P(z, t)$ is referred to as the mean propagator (Kärger and Heink 1983; Callaghan et al. 1991) and denotes the probability (density) that, during the time t , an arbitrarily selected molecule (contributing to the NMR signal) is shifted over a distance z in the direction of the applied field gradient. Under the conditions of normal diffusion (and in a homogeneous system of infinite extension), the mean propagator is a simple Gaussian

$$P(z, t) = (4\pi Dt)^{-1/2} \exp[-z^2/(4Dt)] \quad (2)$$

The parameter D appearing in Eq. (2) is the self-diffusivity which can be equivalently defined (see, e.g., Chapter 2 in (Kärger et al. 2012) or pp. 9–26 in (Kärger 2014a)) either by Fick’s 1st law

$$j^* = -D \frac{\partial c^*}{\partial z} \quad (3)$$

as the factor of proportionality between the flux of labelled molecules and their concentration gradient within an unlabeled surroundings of constant overall concentration or by the Einstein relation

$$\langle z^2(t) \rangle = 2Dt \quad (4)$$

correlating the observation time with the mean square displacement in a given direction. Inserting Eq. (2) into Eq. (1) yields.

$$\frac{S(m, t)}{S(0, t)} = \exp[-m^2 Dt] = \exp\left[-\frac{1}{2} m^2 \langle z^2(t) \rangle\right] \quad (5)$$

With the second equality we have made use of Eq. (4).

Equation (5) serves as a good approach of the PFG NMR signal attenuation even under conditions where the mean propagator is not accurately given anymore by Eq. (2), with diffusion under confinement (see, e.g., (Kärger et al. 1988, Valiullin and Kärger 2016)) as a prominent example. In such cases, the diffusivity D appearing in Eq. (4) has to be understood as an “effective” diffusivity

$$D_{\text{eff}}(t) = \frac{\langle z^2(t) \rangle}{2t} \quad (6)$$

becoming, possibly, a function of the diffusion time, i.e. the separation between the two field gradient pulses. Under the conditions of normal diffusion, D_{eff} is seen to coincide with the genuine self-diffusivity.

2.2 Using the effective diffusivity of PFG NMR as an internal standard

Figure 1 shows, as an example, the Arrhenius plot of the effective diffusivity (ordinate scale on the left-hand side) of water in a bed of crystals of zeolite MFI, following the classical investigations of (Caro et al. 1986). As well given are the root mean square displacements of the guest molecules (ordinate scale on the right-hand side) as resulting from the effective diffusivities via Eq. (6) with the relevant observation time ($t = 1.2$ ms). The measurements have been

Fig. 1 Temperature dependence of the PFG NMR self-diffusivities (D_{eff}) and mean square displacements for water in zeolite MFI: small (open circle, filled circle $\sim 7 \times 4 \times 3$ μm³) and large (open square, filled square $\sim 16 \times 12 \times 8$ μm³) crystals in a loose bed (open sym-

bols) and with the intercrystalline space blocked (filled symbols) for an observation time $t = 1.2$ ms. Reprinted from (Caro et al. 1986), Copyright (1986), with permission from Elsevier

performed with two different crystal sizes, small ones (circles) and large ones (squares). The crystals have, moreover, been applied as loose beds (open symbols) and with the intercrystalline space blocked (filled symbols). The plots are accompanied by cartoon-like representations of the different “micro-dynamic” situations under which the measurements were performed. We may distinguish between three different special cases (for further details, see, e.g., Sect. 11.4 of (Kärger et al. 2012)), namely,

- (i) Genuine intracrystalline diffusion (cartoon on the right), where the crystal sizes notably exceed the diffusion path lengths during the observation time. Observation is thus performed as within crystals of infinite extension.
- (ii) Long-range diffusion (cartoon top left), where the diffusion paths are found to repeatedly cross the intercrystalline space. Under such conditions, the effective diffusivity can approach $p_{\text{inter}}D_{\text{inter}}$, the product of the relative amount of molecules in the intercrystalline space and their diffusivity. D_{inter} significantly exceeds the intracrystalline diffusivity D_{intra} . Therefore, irrespective of $p_{\text{inter}} \ll 1$, $p_{\text{inter}}D_{\text{inter}}$ may notably exceed D_{intra} and even the diffusivity in the bulk liquid under certain conditions (Kärger et al. 1973; D’Orazio et al. 1989).
- (iii) Restricted diffusion (cartoon bottom left), where the guest molecules remain confined to the interior of the individual crystals.

It is, in particular, the latter case of restricted diffusion, which provides us with an independent check of the validity of the PFG NMR diffusivities. For instance, the limiting value of restricted diffusion for spherically shaped particles of radius R is given by the relation

$$D_{\text{eff}}(t) = \frac{R^2}{5t} \quad (7)$$

which, as a rule, serves as a sufficiently good order-of-magnitude test of correctness. Variations in shape appear in slight adjustments to the numerical factor 1/5 (see Sect. 11.4 in (Kärger et al. 2012)).

Equation (7) holds for the limiting case where the diffusion time t is long enough, so that the diffusion path lengths in an infinitely large extended crystal (of the same genuine intracrystalline diffusivity as the crystal under study) would be much larger than the size R of the particle under study. The guest molecules do thus undergo multifold reflections on the external crystal surface, directing them back into the crystal interior.

As another limiting case, where it is as well possible to attain an analytical expression for the time dependence of the effective PFG NMR diffusivity under confinement, one may

consider the situation with observation times t being short enough, so that the mean diffusion path length as resulting with Eq. (4) remains sufficiently small in comparison with the crystal radius. Under such conditions, the effective diffusivity may be given by the relation (Mitra et al. 1992; Mitra and Sen 1992; Geier et al. 2004)

$$\frac{D_{\text{eff}}}{D_0} = 1 - \frac{4}{3\sqrt{\pi R}} \sqrt{D_0 t} \quad (8)$$

with D_0 denoting the genuine intracrystalline diffusivity.

Based on a measurement of the time dependence of the effective PFG NMR diffusivity, Eq. (8) allows the determination of both the genuine intracrystalline diffusivity and the crystal size. Since the latter quantity is as well accessible by microscopic measurement, this limiting case allows a comparison of the outcome of the diffusion measurement with “first-principle” data, namely once again with the crystal sizes.

Figure 2 provides an example of such measurements (Beckert et al. 2013), revealing even two different ranges of observation times reflecting the $\sqrt{t}$ dependence as predicted by Eq. (8). By inspecting the particle morphology (see Fig. 2c), one may easily recognize that the individual host particles represent an agglomerate of smaller crystallites so that, obviously, guest propagation is retarded by two different types of resistances: one is at the mutual interfaces between the individual micro-crystallites (of radius R_{micro}) and the other is at the surface of the particles (of radius R_{particle}). The measurements have been performed with both the water molecules (using, as usual, proton NMR) and with the lithium cations (using ^7Li NMR, at elevated temperature). The radii estimated from the experimentally determined time dependence of the effective diffusivities via Eq. (8) (see the data given in Fig. 2a, b) for water and the lithium cations were found to be of a similar order of magnitude, in the vicinity of what one should expect on also the basis of the micrographs. It is difficult to decide whether differences in the numerical results are indications of genuine differences between the two diffusants or just simple consequences of the uncertainty in measurement.

2.3 Correlating PFG NMR “Tracer” desorption with intracrystalline diffusion

PFG NMR diffusion measurements are commonly performed with fused sample tubes. Temperature enhancement is therefore accompanied by an increase in the gas phase concentration and, hence, in the magnitude of p_{inter} . Thus, by choosing a sufficiently high temperature, it is possible to attain effective (i.e. long-range) diffusivities significantly exceeding the intracrystalline diffusivities. Under such conditions, simple inspection of the PFG NMR signal decay

Fig. 2 Time dependence of the effective diffusivities of water molecules at 25 °C (a) and of the lithium cations at 100 °C (b) in hydrated low-silica zeolite X (Li-LSX) (Schneider et al. 2009) as determined by, respectively, ^1H and ^7Li PFG NMR. Diffusion occurs under confinement within both the adsorbent particles and the crystallites they

consist of (c and d). The best fit of Eq. (8) to the obtained data yields the respective diffusivities and the radii of confinement, as indicated in (a) and (b). Reprinted with permission from (Beckert et al. 2013). Copyright (2013) American Chemical Society

directly yields the relative amount of molecules which, during the chosen observation time, have traveled to another crystal within the bed of crystals under study. PFG NMR thus yields the same information as a conventional tracer experiment, by which one is able to follow the exchange between the (labeled) molecules within a particular crystal and the (unlabeled) ones in the “surroundings”, i.e. in the other crystals and the intercrystalline space. Exchange times accessible in this way are in the range of the PFG NMR observation times which are, depending on the given nuclear magnetic relaxation times, typically between milliseconds and seconds. These are, from the perspective of conventional

tracer exchange measurements (Goddard and Ruthven 1986, Dyer and Faghihian 1998), extremely short time spans so that this technique is as well referred to as “fast tracer desorption” (Kärger 1982, Ruthven 1984).

A useful measure of the rate of molecular exchange between the intracrystalline space and the surroundings is provided by the “first statistical moment” of the tracer exchange curve $F(t)$

$$M_1 = \int_0^1 t dF = \int_0^\infty [1 - F(t)] dt, \quad (9)$$

with $F(t)$ denoting the fraction of molecules having left, during time t , the crystal in which they were initially accommodated. When exchange is exclusively controlled by intracrystalline diffusion, for spherical particles of radius R it holds

$$M_1 = R^2 / (15D_{\text{intra}}) \quad (10)$$

Equation (10) serves, moreover, as a good approach even for particles of any non-spherical shapes if, in Eq. (10)

$$R \equiv 3V/A \quad (11)$$

is understood as the radius of the equivalent sphere with the same surface-to-volume ratio (A/V) as the non-spherical particle under consideration.

With the definition given by Eq. (9) the determination of the first statistical moment is seen to require measurement of signal intensities over time scales notably exceeding the intracrystalline mean life time (or, totally equivalently, the PFG NMR tracer exchange or tracer desorption time). Limitations in measurement accuracy often exclude this possibility. In such cases, as a first-order estimate, intracrystalline mean life times may be determined by approaching the tracer exchange curve $F(t)$ by the expression $1 - \exp(-t/\tau)$, where with Eq. (9) the time constant τ is immediately seen to be the first statistical moment. In a semi-logarithmic presentation versus time, $1 - F(t)$ becomes a straight line with its slope indicating the first statistical moment.

Via Eqs. (9)–(11), PFG NMR tracer desorption experiment thus provides us with an access to intracrystalline diffusivities, which is totally independent of their more “direct” measurement via PFG NMR measurements with diffusion

path lengths much less than the particle diameters. PFG NMR tracer desorption measurements may, therefore, serve as an independent check of the validity of the message of “conventional” PFG NMR. Figure 3 illustrates the potentials and limitations of this technique with the PFG NMR tracer desorption curves of isobutane in various types of zeolite MFI, including two specimens of purely microporous zeolites of different crystal sizes and a mesoporous sample (Mitchell et al. 2012; Machoke et al. 2015; Schwieger et al. 2016) accommodating, within the microporous bulk phase, a network of mesopores (S. Hwang, M. Avramova, T. Weissenberger et al., in preparation).

The measurement results are seen to follow the trends as predicted by Eq. (10) for the interrelation between the intracrystalline mean life times (= time constants of molecular exchange M_1), the crystal sizes and the intracrystalline diffusivities. On comparing the intracrystalline mean life times, the incorporation of a network of transport pores within the microporous bulk phase is indeed found to lead to a dramatic acceleration of the intracrystalline diffusivities, giving rise to a corresponding enhancement in molecular exchange rates. Comparison of the intracrystalline mean life times in the purely microporous samples does as well reflect the behavior as expected with Eq. (10), where the intracrystalline mean life time is predicted to increase with the square of the crystal size.

This conclusion implies coincidence of the intracrystalline diffusivities in the two samples. Zeolites of type MFI, however, are known to appear in various topological modifications (Karwacki et al. 2009; Vasenkov and Kärger 2002) with, correspondingly, differing intracrystalline diffusivity.

Fig. 3 PFG NMR Tracer-Desorption curves (i.e. representation of the relative amount $1 - F(t)$ of guest molecules which, after time t , have not yet left the crystals in which they were initially accommodated) for isobutane at room temperature, determined for three different types of zeolite MFI, namely purely microporous silicalite-1 crystals with a mean diameter of about 1 μm (filled squares) and 0.7

μm (filled circles) and mesoporous silicalite-1 crystals with a diameter of about 1 μm (open squares). The straight lines are approaches of the decay to the function $\exp(-t/\tau)$. They have been used for a first-order estimate of the molecular exchange time (i.e. the first statistical moment M_1) of the PFG NMR trace-desorption curve as also indicated

Therefore, coincidence in the diffusivity of different samples cannot be expected to be necessarily true and should be confirmed in separate PFG NMR investigations. Such measurements, however, had not been possible with the samples under study, notably as a consequence of their rather limited size. In previous PFG NMR studies, intracrystalline diffusivities of isobutane in zeolite MFI were found to be of the order of $10^{-12} \text{ m}^2\text{s}^{-1}$. By inserting this value into Eq. (10), intracrystalline mean life times in the purely microporous samples are estimated to be of the order of tens of milliseconds and, hence, by about one order of magnitude smaller. It has remained the topic of ongoing work (S. Hwang, M. Avramova, T. Weissenberger et al., in preparation) to decide whether this difference is attributed to, e.g., the existence of surface barriers as one of the most likely explanations of the difference.

3 Microimaging

3.1 Unambiguous diffusion measurement by monitoring the evolution of concentration profiles

Transport diffusivities D_T are defined via Fick's 1st law

$$j = -D_T(c) \frac{\partial c}{\partial z} \quad (12)$$

as the factor of proportionality between molecular fluxes and the underlying gradients in molecular concentration (Price 2009; Kärger et al. 2012; Kärger and Ruthven 2016). With the notation of Eq. (12) the transport diffusivity $D_T(c)$ is explicitly indicated to be a function of the given concentration c . This is different from the situation considered with the notation of Fick's 1st law in Eq. (3) for the definition of the self-diffusivity D which is clearly independent of how many molecules (among the constant, total amount of molecules) are labelled, i.e. of c^* . Combining Eq. (12) with the continuity equation,

$$\dot{c} = -\frac{\partial j}{\partial z} \quad (13)$$

yields Fick's 2nd law:

$$\dot{c} = \frac{\partial}{\partial z} \left[D_T(c) \frac{\partial c}{\partial z} \right] \quad (14)$$

For measurement over sufficiently small concentration intervals so that $D_T(c)$ over the interval may be considered to remain constant, Eq. (14) can be written as the simpler, more commonly cited form

$$\dot{c} = D_T \frac{\partial^2 c}{\partial z^2} \quad (15)$$

This form of Fick's 2nd law, with $c = c^*$ and with the self-diffusivity D replacing the transport diffusivity D_T , holds especially in the case of self-diffusion/tracer exchange where the diffusivity is constant throughout the crystals/particles and only depends on the overall concentration (of labelled plus unlabeled molecules) rather than on the concentration c^* of the labelled species.

Following Eqs. (12)–(15), direct measurement of the distribution of guest concentrations in the interior of the crystals/particles under study and of their variation with time provides the most direct access to the underlying diffusivities. Among the manifold techniques allowing such monitoring, imaging by nuclear magnetic resonance has, most likely, attained largest popularity (Gladden et al. 2008; Kahn and Busse 2012; Willis et al. 2018), notably due to its unprecedented potentials for application in medical diagnosis. Since the very first applications of “nuclear magnetic imaging” (at this time still under the name “zeugmatography” as coined by its inventor, Paul Lauterbur (P.C. Lauterbur 1973)) there have been intense efforts of monitoring molecular concentrations in beds of zeolite crystallites (Heink et al. 1978), see also Sect. 12.1.5 in (Kärger et al. 2012). Spatial and temporal resolution, however, did not suffice to monitor the evolution of intracrystalline concentration profiles. This has remained to be essentially true till even today, irrespective of dramatic progress in MR imaging over the last few decades (Stapf and Han 2006; Lysova and Koptiyug 2010).

The decisive breakthrough came with the advent of interference microscopy (IFM) and infrared microscopy (IRM) as the techniques of choice for monitoring the evolution of the distribution of guest molecules within nanoporous crystals/particles (Heinke et al. 2007, Kärger et al. 2014), Sect. 12.2 in (Kärger et al. 2012). Both techniques provide direct access to the concentration integral in observation direction, with a spatial resolution below micrometers (IFM) and of a couple of micrometers (IRM) on the observation plane. Temporal resolutions so far attained are of the order of seconds (IFM) and tens of seconds (IRM). IFM measurements are based on the fact that the refractive index of the nanoporous solid under study is a (monotonic) function of the guest concentration and that (concentration-induced) changes in the refractive index appear (and may hence be quantified) in the interference pattern with a reference beam. In IRM, information about the concentration of a certain molecular species is attained by recording the intensity of its characteristic absorption band in the IR beam transmitted through the crystal/particle under study. IRM does therefore allow the simultaneous observation of various components, while

Fig. 4 **a** Evolution of the transient concentration of cyclohexane in a nanoporous glass during molecular uptake induced by a pressure step from 0 to 0.1 mbar in the surrounding atmosphere, recorded by IRM (circles) at 298 K and comparison with the predictions (solid lines) as resulting from the solution of Fick's 2nd law, Eq. (14), with the rel-

evant initial and boundary conditions. **b** Concentration dependence of the transport diffusivity as implied for the prediction of the concentration profiles shown in (a). Reproduced from (Titze et al. 2015b), with permission from John Wiley and Sons

distinguishing them, which makes this technique particularly useful for diffusion studies during catalytic conversion (Titze et al. 2015a; Chmelik et al. 2018).

Figure 4 provides an example of the agreement between the measurement of transient concentration profiles obtained via microimaging by IRM and the predictions by Fick's 2nd law. Such measurements are seen to serve, simultaneously, as an independent confirmation of the validity of Fick's 2nd law for the host–guest system under consideration.

3.2 Correlating diffusion measurement with adsorption thermodynamics

The exploration of correlations between molecular diffusion and adsorption continues to be a hot topic in sorption sciences (Krishna et al. 1999; Keil et al. 2000; Krishna and van Baten 2013). Interest in such correlations is largely generated by the fact that the parameters describing adsorption equilibria are, as a rule, attainable with much larger accuracy and reliability than non-equilibrium parameters like the various diffusivities. Given the fundamental difference between equilibrium and non-equilibrium phenomena (Prigogine 1997), there is no direct path along which equilibrium data might be transferred into non-equilibrium ones like diffusivities. With the Transition State Theory (TST) (Gladstone et al. 1941), however, we dispose of a formalism by which, under certain conditions, some features of non-equilibrium thermodynamics may become indeed predictable on the basis of the information exclusively collected

by equilibrium measurement (Ruthven and Derrah 1972; Kärger et al. 1980). Coincidence of the messages provided by two totally independent techniques would thus serve as a strong argument confirming the reliability of the results revealed by either of them.

As a prerequisite of the application of TST to diffusion in nanoporous materials, molecular propagation must be controlled by molecular passages through the “windows” connecting adjacent cavities. These passages or “jumps” are considered as infrequent events (see, e.g., Chapter 9 in (Kärger et al. 2012)) so that, at a given instant of time, molecular passages occur only in quite a small number of windows, definitely not several ones in one and the same window and scarcely in adjacent ones. During the window passage, the molecules are moreover implied to be isolated from the remaining ones. With the equilibrium conditions for dynamic exchange between the molecules in the cavities (“ground state”) and those in the windows (“activated state”), molecular mean lifetime within a cavity may be noted to obey the following relation (Chmelik and Kärger 2016)

$$\frac{1}{\tau(c)} \propto \frac{p(c)}{c} \quad (16)$$

where, according to the conception of TST, the mean lifetime in the activated state is implied to be independent of concentration. Since occupation of the windows is a rare event, their population may be assumed to be proportional to the pressure p in the surrounding atmosphere.

For diffusion by jumps, following the dependences as appearing in already the Einstein relation, Eq. 4, it holds

$$D(c) \propto \frac{l^2}{\tau(c)} \quad (17)$$

with l denoting the (effective) mean jump length which, in the present case, is given by the separation between adjacent cavities. Combination of Eqs. (16) and (17) yields

$$D(c) \propto \frac{p(c)}{c} \quad (18)$$

For propagation by jumps the correlation between self- and transport diffusion (see, e.g., Sect. 2.5 of (Kärger et al. 2012) and (Lauerer et al. 2015a, b) for also two-component diffusion) is given by the relation

$$D_T = \frac{d}{dc}[c \times D(c)] \quad (19)$$

which, in combination with Eq. (18), yields

$$D_T(c) \propto \frac{\partial p(c)}{\partial c} \quad (20)$$

For sufficiently small concentrations where any interaction between the guest molecules can be neglected, the transport and self-diffusivities coincide, which may easily be rationalized by the fact that it is the interaction which makes the difference between equilibrium and non-equilibrium conditions (Prigogine 1997). Equations (18) and (20) can thus be rewritten as

$$D = D(c=0) \times k \frac{p(c)}{c} \quad (21)$$

and

$$D_T = D(c=0) \times k \frac{dp}{dc} \quad (22)$$

with the self-diffusivity at vanishing concentration (coinciding with the transport diffusivity) as the common factor of proportionality. k stands for the Henry coefficient: $k \equiv \left(\frac{c}{p}\right)_{c \rightarrow 0} = \left(\frac{\partial c}{\partial p}\right)_{c \rightarrow 0}$

We note, on passing, that combination of eqs. (21) and (22) yields the relation

$$D_T = D \frac{d \ln p}{d \ln c} \quad (23)$$

with $\frac{d \ln p}{d \ln c}$ referred to as the thermodynamic (correction) factor. The identical relation (with D replaced by D_0) is known as the defining equation for the “corrected” or “Stefan-Maxwell” diffusivity. It has been introduced as a quantity where the influence of thermodynamics as appearing in the factor $\frac{d \ln p}{d \ln c}$ in the transport diffusivity is explicitly taken account

of (Ruthven 2008; Krishna 2009, 2014; Kärger et al. 2012; Kärger and Ruthven 2016). With Eq. (23) it appears that, under the conditions of “narrow-pore” diffusion, corrected diffusivities and self-diffusivities coincide. In more open pore structures, the corrected diffusivities are known to exceed the self-diffusivities.

Figure 5 provides an example where the application of TST to an a priori prediction of the concentration dependence of guest diffusion in nanoporous materials yielded an astonishingly good agreement with the outcome of preceding experimental measurement by IRM (Chmelik 2015). IRM is applicable with, essentially, identical experimental configuration to both uptake and tracer exchange measurements, allowing the simultaneous determination of transport and self-diffusivities. Agreement between the experimental data and the theoretical predictions confirms the validity of the introduced formalism. It resembles, in a sense, the hierarchical simulation approach of ref. (Tallarek, et al. 2019) successfully correlating interfacial (thermo-) dynamics with structure-related molecular kinetics. Up to which extent the proposed reasoning is applicable to further systems is primarily a question of the availability of the necessary data sets. Owing to an impressive increase in the number of nanoporous host systems, investigations along these lines should be also a promising undertaking in the near future.

4 Conclusions

Molecular diffusion is a key phenomenon determining the rate of mass transfer into and out of nanoporous materials. It thus significantly affects the performance of many technological processes grounded on the application of such materials. The fact that diffusion coefficients are only one parameter in a large ensemble of different influences makes their measurement a particularly challenging task and it is often unclear whether diffusion data provided in the literature do, in fact, refer to those processes to which they are claimed to refer.

As a consequence, the availability of a tool box offering different techniques of measurement is clearly more than welcome. Such a tool box is in fact available by a suitable combination of various techniques of diffusion measurements and there are several examples where different measurement techniques, including both the so-called “microscopic” and “macroscopic” ones, yield satisfactory agreement (Jobic et al. 2005; Kärger et al. 2009; Chmelik et al. 2011). In the present communication, we were looking for an alternative pathway to confirm the attained diffusivity data by comparing with the information provided by other measuring techniques beyond the field of diffusion.

Fig. 5 Results of the experimental measurement of transport diffusivities (D_T , squares), corrected transport diffusivities (D_0 , filled circles) and self-diffusivities (D , open circles) of various guest molecules (**a** ethene, **b** ethane, **c** propene, **d** propane, **e** methanol; **f** ethanol) in MOF ZIF-8 single crystals by IRM in combination with measure-

ment of the adsorption isotherms and comparison with the concentration dependences predicted via TST by Eqs. (21) and (22) (full lines). Reprinted from (Chmelik and Kärger 2016), Copyright (2016), with permission from Elsevier

Although such an approach can probably lead to important new findings for, essentially, any experimental techniques, it seems to be particularly effective for the “microscopic” methods. In this context, we could notably refer to the potentials of PFG NMR. Depending on the given experimental situation, PFG NMR is able to trace diffusivities together with characteristic spatial extensions of the samples as crystal diameters. The latter ones provide an excellent

object for independent measurement and, hence, for independent confirmation of the diffusivity data.

Being sensitive to concentrations and their variation in space and time, microimaging by IRM and IFM keeps its focus squarely on these phenomena, which via Fick’s relations give rise to the diffusivities. In addition to a remarkable enhancement in data quality and reliability, microimaging has also given rise to a dramatic enhancement in the data

output, including information about both transport diffusion (via uptake and release) and self-diffusion (via tracer exchange). With such data, obtained with short hydrocarbons in MOF ZIF-8 as a standard “narrow-pore” metal organic framework, the classical transition state theory (TST) was found to predict the concentration dependence with astonishing accuracy, providing us with independent experimental evidence for the validity of the diffusivity data obtained by IRM.

With these examples, however, it becomes also obvious that such comparative studies are far from straightforward and only applicable under, so far, limited conditions. These include, in particular, the availability of host material of suitable size, i.e. sufficiently large crystals/particles (of typically 10 μm or more) for PFG NMR and well-shaped particles of at least such size (ideally as thin plates with sealed top and bottom surfaces) for microimaging. Given the relevance of diffusion as a key parameter in numerous matter upgrading technologies and as one of the most fundamental phenomena in nature, continued efforts in qualifying the potentials of diffusion measurements, including their unambiguous validation, are highly wanted.

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Data availability Not applicable

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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