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Diffusion in nanoporous materials with special consideration of the measurement of determining parameters (IUPAC Technical Report)

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Abstract: The random motion (the diffusion) of guest molecules in nanoporous host materials is key to their manifold technological applications and, simultaneously, a ubiquitous phenomenon in nature quite in general. Based on a specification of the different conditions under which molecular diffusion in nanoporous materials may occur and of the thus resulting relevant parameters, a survey of the various ways of the measurement of the determining parameters is given. Starting with a condensed introduction to the respective measuring principles, the survey notably includes a summary of the various parameters accessible by each individual technique, jointly with an overview of their strengths and weaknesses as well as of the respective ranges of observation. The presentation is complemented by basic relations of diffusion theory and molecular modeling in nanoporous materials, illustrating their significance for enhancing the informative value of each measuring technique and

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the added value attainable by their combination. By providing guidelines for the measurement and reporting of diffusion properties of chemical compounds in nanopores, the document aims to contribute to the clarification and standardization of the presentation, nomenclature, and methodology associated with the documentation of diffusion phenomena in nanoporous materials serving for catalytic, mass separation, and other relevant purposes.

Keywords: Mass transfer; nanostructured materials; physical and biophysical chemistry division.

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1 Introduction

The random motion of the constituents of matter, notably of atoms, ions, and molecules, is among the most widespread phenomena in our world. It is the basis of our life and key to numerous technological processes, determining their performance and functionality. This phenomenon is commonly referred to as diffusion.

The rate of diffusion and, related to it, the options of its quantification depend on the nature of the system under consideration. Diffusion phenomena in fluids occur at much higher rates than in solids and require, correspondingly, completely different devices for their investigation. For the quantification of diffusion phenomena, there exist well-defined guidelines. The resulting quantities are, as a rule, referred to as diffusion coefficients or, essentially synonymously, as diffusion constants, coefficients of diffusion, or diffusivities. Depending on the particular measurement conditions, these variables are, as a rule, additionally specified by an attribute. The coefficients of guest diffusion in nanoporous host materials cover a broad range, essentially between those in liquids and solids. Capturing such a wide range of mobilities is scarcely achievable with a single technique and necessitates, in general, the application of a multitude of different measuring techniques.

In addition to the type and density of the guest molecule and the temperature, guest diffusivities most significantly depend on the pore structure of the host. For the classification of porous materials and the options of exploration of their pore structure, see, for example, the IUPAC Recommendations by McCusker *et al.*¹ and the IUPAC Technical Reports by Rouquerol *et al.*^{2,3}

Following Thommes *et al.*,⁴ materials with pore widths up to 100 nm are referred to as nanoporous. Nanopores is an umbrella term that includes micropores (pore width up to 2 nm), mesopores (2 to 50 nm), and macropores (pore widths above 50 nm, with only those up to 100 nm also referred to as nanopores). We are going to use the terms nanoporous material and nanoporous adsorbent essentially synonymously, where in the latter case, for the sake brevity, the specification “nanoporous” is generally omitted. For a full comprehension of mass transfer in nanoporous materials, diffusion pathways must be followed from the elementary steps of diffusion up to distances far beyond the width of the individual pores, that is, possibly up to hundreds of micrometers. This is another reason for the diversity of the measurement techniques employed for quantifying mass transfer in nanoporous materials.

This necessity is further enhanced since mass transfer over essentially all distances may be rate limiting for the overall process and may thus determine the performance of a wide variety of technological applications of nanoporous materials, ranging from chemical conversion, separation, purification, and capture to energy storage and fuel cell applications. The exploration of diffusive mass transfer in nanoporous materials is thus not only a challenging task of fundamental research, aiming at an understanding of host–guest interaction on solid surfaces, but may as well be crucial for a theory-based optimization of the technological application of these materials.

Over the course of the last few decades, progress in existing and new measuring techniques, in parallel with the development of novel concepts of theoretical prediction and molecular modeling, has opened up the potential for a comprehensive understanding of diffusion phenomena in nanoporous materials, covering the various space

and time scales of relevance for mass transfer. First surveys covering the field have been provided by several textbooks.^{5,6} Benefitting from a recent compilation of papers^{7,8} dedicated to the various experimental techniques applied for studying diffusion in nanoporous materials, following preceding summarizing accounts,^{9–13} the present communication is intended to provide a first comprehensive set of guidelines for the measurement and the reporting of the determining parameters for the diffusion of chemical compounds in nanoporous materials serving for catalytic, mass separation, and other relevant purposes.

The treatise starts, in Section 2, with a presentation of the terminology used for the quantification of the determining parameter for diffusion in nanoporous materials, with the diffusion coefficient as its central parameter. Depending on the host material and the chosen experimental conditions, this parameter may appear in different variants. Transport barriers, possibly acting in addition to the diffusional resistance of the genuine pore space both in the material bulk phase and on the external particle/crystal surface, are as well considered. Section 3 provides an overview of the various measurement techniques applied for the quantification of guest diffusion in nanoporous materials, with a particular emphasis on their limitations and risks of misinterpretation. Examples of the beneficial corroboration of experimental measurement from molecular simulation (and vice versa) are presented in Section 4. The paper concludes with a summary of the various experimental techniques used for the investigation of guest diffusion in nanoporous materials, notably including their strengths and weaknesses.

2 Diffusion fundamentals in nanoporous materials: definitions and terminology

2.1 Pore space viewed as a homogeneous continuum

Diffusion of guest molecules in nanoporous host materials is commonly quantified via Fick's 1st law by correlating molecular fluxes with the concentration gradients giving rise to their emergence. It is illustrated by Fig. 1a and b that, with the formation of gradients $\frac{dc}{dx}$ in the concentration c , one may follow two different scenarios. Figure 1a considers a non-equilibrium situation, with the resulting net flux j directed toward lower concentration, giving rise to the following notation:

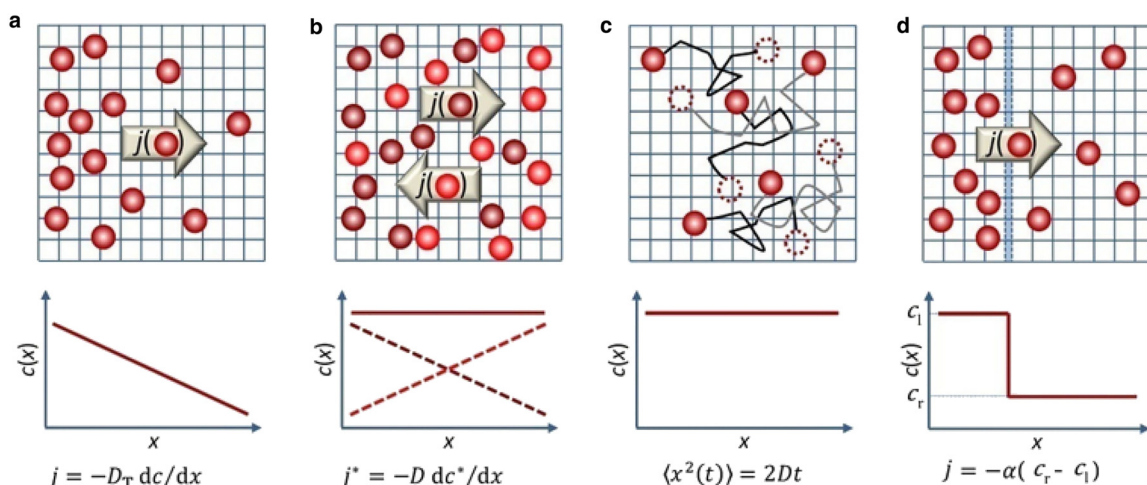


Fig. 1: Schematic representations of the measurement of diffusion coefficients in nanoporous materials (a: transport diffusivity by fluxes; b: self- or tracer diffusivity by fluxes; c: self- or tracer diffusivity by mean square displacements; d: barrier permeabilities by fluxes). Adapted from Kärger *et al.*⁸ with permission.

$$j = -D_T \frac{dc}{dx}. \quad (1)$$

The factor of proportionality D_T is referred to as the coefficient of transport (hence the subscript T) diffusion (or transport diffusivity). In use are also the terms Fickian or chemical diffusivity. A summary and explanation of all symbols can be found in a glossary at the end of this report.

As indicated by the differences in their shading, with Fig. 1b we consider two different types of molecules, which, however, are implied to be indistinguishable in their microdynamic properties. Experimentally, such a situation may be approached by isotopic substitution of one or more of their atoms. In place of Eq. 1, with

$$j^* = -D \frac{dc^*}{dx} \quad (2)$$

one now correlates the fluxes of the differently labeled molecular species and their concentration gradients. The asterisks refer to the flux, j^* , and the concentration, c^* , of one of the two constituents.

Once again, the molecular fluxes may be expected to be proportional to the concentration gradients that give rise to them. However, there is a significant difference in the microdynamic situation as “experienced” by the molecules: While molecular migration in Fig. 1b occurs under overall equilibrium, the existence of the concentration gradient in Fig. 1a gives rise to a different microdynamic situation. One cannot imply, therefore, that the proportionality factors appearing in Eqs. 1 and 2 must coincide. In Fig. 1b and Eq. 2, the proportionality factor D is therefore referred to as the self- or tracer diffusivity.

The need of differentiation between transport and self-diffusion vanishes in the limiting case of sufficiently small guest concentration, when the influence of mutual molecular encounters becomes negligibly small. This is a consequence of the more general rule that a distinction between equilibrium and non-equilibrium phenomena in a system becomes meaningless in the absence of molecular interactions.¹⁴

Proportionality between the fluxes and the concentration gradients as implied by Eqs. 1 and 2 is inherent to the measuring principle of self-diffusion. On considering transport diffusion, it poses some upper limit to the concentration gradient. These limitations, however, are far beyond the case of practical relevance with concentration gradients of typically (or even less than) a few molecules per cubic nanometer over distances of micrometers.

Equations 1 and 2 are key to a most direct determination of diffusivities, namely, by simultaneous measurement of the given concentration gradients and molecular fluxes emerging under their influence.

Numerous techniques of diffusion measurement are based on the observation of a diffusion-induced variation in guest concentration. The analytical basis of such an analysis is provided by Fick's 2nd law. It results by combining Fick's 1st law with the law of matter conservation (the “continuity equation”),

$$\frac{\partial c^{(*)}}{\partial t} = -\frac{\partial j^{(*)}}{\partial x}, \quad (3)$$

holding for both, all molecules (c, j) and the labeled ones (c^*, j^*). The continuity equation states that an imbalance between incoming flow and outgoing flow ($\frac{\partial j^{(*)}}{\partial x} \neq 0$) gives rise to a temporal variation in local concentration.

Under the conditions of tracer exchange (i.e., on considering the counter fluxes of differently labeled, but otherwise identical molecules), inserting Fick's 1st law into Eq. 3 yields the following equation:

$$\frac{\partial c^*}{\partial t} = D \frac{\partial^2 c^*}{\partial x^2}, \quad (4)$$

where Fick's 2nd law assumes a particularly simple form. On notating Eq. 4 we have benefitted from the fact that, during a tracer exchange experiment (Fig. 1b), the overall concentration and, hence, also the diffusivity are uniform all over the sample, that is, independent of the location x . It is due to this reason that, when considering tracer exchange, the (self-) diffusivity appears as simply a factor on the right-hand side of Fick's 2nd law instead of appearing inside the derivative (see Eq. 7).

Equation 4 is key to the understanding of a second route toward the experimental determination of the self-diffusivity. It is based on the measurement of the mean square displacement of the molecules under overall equilibrium (Fig. 1c).

An expression for the probability $P(x, t)$ that a molecule, initially at position $x = 0$, has reached position x at time t can be obtained as the solution of Eq. 4 in an infinitely extended medium, with the initial condition given by Dirac's delta function $c^*(x, t = 0) = \delta(x)$, that is, by assuming that all labeled molecules are initially situated in the origin, at $x = 0$. The Gaussian

$$P(x, t) = (4\pi Dt)^{-1/2} \exp\left(-\frac{x^2}{4Dt}\right) \quad (5)$$

is easily recognized as the desired solution of Eq. 4. The mean square displacement of the guest molecules during an observation time t may thus be calculated to be

$$\langle x^2(t) \rangle \equiv \int_{-\infty}^{\infty} x^2 P(x, t) dx = 2Dt. \quad (6)$$

Here and in following equations, we use the physical convention that angle brackets denote the expectation value of a random variable. The detection of the equivalence of Eqs. 2 and 6 in the quantification of self-diffusion was one of Einstein's great discoveries in his *annus mirabilis* 1905.^{15–17}

Experimental techniques that are capable of following the diffusion path of the individual guest molecules are thus seen to open up, via Eq. 6, an alternative way toward the determination of self-diffusivities. As a consequence of the Ergodic theorem of statistical physics,¹⁸ it should be of no relevance whether the averaging is performed over all molecules over one and the same time interval or over successive time intervals for one and the same molecule. Experimental confirmation of this postulate for guest molecules in nanoporous materials was provided by Feil *et al.*¹⁹

Equation 5 may as well be understood to emerge as a special case of the central limit theorem of statistics,²⁰ which predicts that the superposition of elementary "steps" with identical probability distributions will always lead to a probability distribution given by a Gaussian.

Under the conditions of transport diffusion, that is, under the influence of internal overall concentration gradients, combination of Fick's 1st law, Eq. 1, with the continuity equation, Eq. 3, gives rise to Fick's 2nd law in the following form:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D_T \frac{\partial c}{\partial x} \right) = D_T \frac{\partial^2 c}{\partial x^2} + \frac{dD_T}{dc} \left(\frac{\partial c}{\partial x} \right)^2. \quad (7)$$

Equation 7 contains, in addition to the notation of Fick's second law under tracer exchange, Eq. 4, a second term on the right-hand side. It takes into account that the differences in local concentration also give rise to differences in the local diffusivities. This term, obviously, disappears as soon as the range of diffusivities covered during the experiment is sufficiently small. Such a situation may be approached by choosing, in the uptake or release experiment, a sufficiently small pressure step.

In addition to the effect of the genuine pore space of the individual sorbent particles/crystals, molecular fluxes may as well be affected by transport resistances originating from deviations in the regular pore structure and from depositions both in the sorbent interior and on their external surface. This is the situation illustrated by Fig. 1d for transport barriers in the sorbent interior (for "internal barriers"). They are quantified by following the relation:

$$j = -a(c_{x^+} - c_{x^-}) \quad (8)$$

with the parameter a (referred to as the barrier permeability) appearing as the factor of proportionality between the flux j through the barrier and the difference in the concentrations immediately before and after the internal barrier, c_{x^+} and c_{x^-} , respectively. The flux direction is parallel to the x -axis but with a negative sign, consistent with the definition of the diffusion flux.

For transport resistances on the sorbent surface it holds, correspondingly,

$$j = -\alpha[c_{\text{eq}} - c_r] \quad (9)$$

with c_{eq} and c_r denoting, respectively, the concentrations at equilibrium with the surrounding atmosphere and close to the boundary of the sorbent (of thickness $2l$). Here, the parameter α is referred to as the surface permeability.

Owing to the possible existence of surface barriers, the rate of molecular uptake or release on a single crystal/particle as accessible by, for example, microimaging (see Section 3.8) or fast tracer desorption Nuclear Magnetic Resonance (NMR) (see Section 3.11) may thus be controlled by both intracrystalline diffusion and surface permeation, depending on their relative influences. A convenient means for discrimination is provided by the method of the “first statistical moment,” M_1 , in uptake measurement.^{6,13,21,22} In analogy to the use of moments’ analysis in Adsorption Column Dynamics (see Sections 3.2 and 3.5), it is defined by the following relation:

$$M_1 = \int_0^1 t dF = \int_0^\infty [1 - F(t)] dt \quad (10)$$

with $F(t)$ denoting the fractional uptake or release at time t . For a sphere of radius R with transport limited by the intracrystalline transport diffusivity D_T , for example, it is given by the relation

$$M_{1,\text{dif}} = R^2 / (15D_T). \quad (11)$$

Equation 11 allows a reasonable estimate of the uptake or release time for an adsorbent crystal/particle of arbitrary shape if R is understood as an effective radius (the “characteristic dimension”) via the relation.

$$R = \frac{3V}{A} \quad (12)$$

with V and A denoting, respectively, the volume and surface area of the crystal/particle under study.

The ratio.

$$\frac{R^2}{D_T} = t_{\text{dif}} \quad (13)$$

(i.e., the ratio of the square of the characteristic dimension and the diffusion coefficient) is commonly referred to as the “diffusion time.”

As the equivalent of Eq. 11, one obtains, under limitation by a surface barrier permeability, α ,

$$M_{1,\text{sur}} = R / (3\alpha). \quad (14)$$

If both influences are important, the first moment simply results as the sum of both expressions.

As a matter of course, all so far considered equations can only be meaningful, if the quantities appearing in these equations are meaningful as well. This means that the unit volumes for defining the guest concentrations and the unit areas for defining the guest fluxes notably exceed the dimensions of the individual pores and are, moreover, chosen to be large enough so that, in a statistical sense, they may be assumed to be identical. The pore space is thus assumed to form a homogeneous continuum. Consequences of systematic variations in the structural properties shall be considered in Sections 2.2 and 4.2.

So far, the systems under study have implicitly been assumed to be isotropic. Therefore, we could restrict ourselves to considering diffusion in an arbitrarily selected direction. However, many nanoporous, notably crystalline, materials are known to be of anisotropic structure. Fick’s 1st law, Eq. 1 (and, correspondingly, also Eq. 2), must hence be replaced by a more general expression

$$\vec{j} = -\vec{D}_T \text{grad } c \quad (15)$$

with the diffusion coefficient replaced by the diffusion tensor. Because of the direction dependence of the diffusivity, fluxes are now not anymore necessarily oriented in parallel to the concentration gradient. It is always

possible, however, to find a coordinate system, in which the diffusion tensor assumes a diagonal form. In such a system (with the coordinates coinciding with the “principal directions” of the diffusion tensor), Eq. 15 assumes the shape of Eq. 1 with

$$j_i = -D_{Ti} \frac{\partial c}{\partial x_i}, \quad (16)$$

where the D_{Ti} are the principal diffusivities, that is, the elements of the diagonalized diffusion tensor. Fick’s second law (in the notation with a negligible influence of the concentration dependence of the diffusivity) becomes

$$\frac{\partial c}{\partial t} = \sum D_{Ti} \frac{\partial^2 c}{\partial x_i^2}. \quad (17)$$

In most practical cases, nanoporous materials host a mixture of guest molecules rather than a single species. Then the flux of each individual component becomes a linear combination of all concentration gradients (with the subscripts i and j now referring to the individual species)

$$j_i = -\sum_j D_{ij} \frac{\partial c_j}{\partial x}. \quad (18)$$

The diffusion coefficient has now become a diffusion matrix, with the element D_{ij} denoting the influence of the gradient of the j -th species on the flux of the i -th species. The elements of the diffusion matrix are, in general, a function of the concentration of all species, with the concentration gradients of all components affecting all fluxes.

Once again, the situation notably simplifies for sufficiently low concentrations, where the diffusion matrix becomes diagonal:

$$D_{ij} = \delta_{ij} D_i \quad (19)$$

where $\delta_{ij} = 1$ for $i = j$ and is otherwise equal to 0 and the transport and self-diffusivities coincide.

All features of diffusion so far considered could be rationalized by following the random walk of the guest molecules as illustrated in Fig. 1. Deeper understanding is facilitated by incorporating the role of the gradient of the chemical potential ($-\frac{d\mu}{dx}$) as the driving force of diffusion. By adopting the Maxwell–Stefan model^{23,24} to diffusion in nanoporous materials, this option has notably been explored and exploited in greater detail by Krishna and co-workers.^{25–27}

If diffusion is interpreted as a result of the gradient of the chemical potential as the driving force of the diffusion motion, the mean velocity u of the diffusive flux may be written in the following form:

$$fu = -\frac{d\mu}{dx} \quad (20)$$

with the friction coefficient f representing the resistance experienced by the guest molecules on their diffusion path. With the adsorption isotherm $c(p)$, we can also eliminate the chemical potential from the expressions:

$$\mu(c) = \mu_0 + R_g T \ln \left[\frac{p(c)}{p(c_0)} \right], \quad (21)$$

where R_g stands for the gas constant and μ_0 denotes the chemical potential for a reference concentration c_0 . We are, moreover, using the ideal-gas approximation with the pressure p serving as a sufficiently accurate substitute of the fugacity.

The product of the guest concentration c with the mean guest velocity u provides an expression for the diffusive flux

$$j \equiv uc = -\frac{R_g T}{f} \frac{(c/p)}{(dc/dp)} \frac{dc}{dx}. \quad (22)$$

Comparison of this relation with Fick's 1st law, Eq. 1, yields the following equation:

$$D_T = \frac{R_g T}{f} \frac{(c/p)}{(dc/dp)} = D_c \frac{(c/p)}{(dc/dp)}, \quad (23)$$

with D_c referred to as the “corrected” or Maxwell–Stefan diffusivity. The transport diffusivity is thus split into two factors. The term $\frac{(c/p)}{(dp/dc)}$, referred to as the “thermodynamic factor,” is exclusively related to the adsorption isotherm, becoming different from 1 for adsorption isotherms deviating from linearity. The second factor $\frac{R_g T}{f}$ is, via the term $1/f$, exclusively a measure of the molecular mobility. Both terms vary with varying concentrations, with the concentration dependence of the transport diffusivity commonly exceeding the concentration dependence of the corrected diffusivity. Eq. 23 is referred to as the Darken equation.

On considering mass transfer in cylindrical pores, that is, in microporous materials of one-dimensional pore structure (see, e.g.²⁸, with more than 50 zeolite structure types with one-dimensional channels) one has to be aware of the particular situation that may arise as soon as the considered guest molecules are too large to pass one another in the pores. This type of mass transfer is referred to as single-file diffusion (see, e.g.^{29–31}, and Section 5 of Kärger et al.⁶) and known to exhibit features that may notably deviate from those of “normal diffusion” so far considered.

It is true that, under the conditions of transport diffusion as illustrated with Fig. 1a, this type of additional confinement leaves the formalism based on the introduction of the transport diffusivity via Eq. 1 unaffected.³² This can intuitively be understood quite easily by realizing that transport diffusion exclusively proceeds by an exchange between occupied sites and neighboring unoccupied ones, which occurs independently of whether molecular exchange between occupied neighboring sites is possible or not.³²

However, on considering tracer exchange (Fig. 1b) or the propagation probability of selected molecules (Fig. 1c), confinement within a single-file system gives rise to totally different transport patterns. This is most easily demonstrated for molecular propagation in an infinitely extended single-file system. Here, subsequent displacements of a selected molecule within a chain of molecules are more likely directed in opposite directions, and this tendency increases with increasing displacements. This is a simple consequence of the fact that, with increasing displacement, the probability for higher guest densities “in front of” the considered molecule increases, while the opposite is true in the other direction. This anti-correlation in subsequent molecular displacements violates the preconditions of the applicability of the central limit theorem so that, consequently, molecular mean square displacements cannot be expected to increase in proportion with the observation time as, with Eqs. (5) and (6), is the case for normal diffusion. It may rather be shown that confinement to an infinitely extended “single file” gives rise to molecular mean square displacements increasing with only the square root of time.^{29,30,33–35}

In the present context we deal with single-file systems of finite length, given by the size of the nanoporous crystals accommodating the channels under consideration. As a consequence, we have to consider molecular exchange between boundary sites and the surrounding atmosphere as a second mechanism giving rise to molecular displacements. The mean square values of these displacements increase in proportion with the observation time. Thus, even for displacements negligibly small in comparison with the file size, this mechanism becomes the dominating one, with a mean square displacement given by the following relation.^{31,36,37}

$$\langle (\Delta x)^2 \rangle = 2D_{\text{iso}} \frac{1-\theta}{\theta} \frac{\lambda}{L} t = 2D_{\text{iso}} \frac{1-\theta}{n} t. \quad (24)$$

$D_{\text{iso}} = \lambda^2/(2\tau)$ stands for the self-diffusivity of an isolated molecule within the file. The L , n , λ , and τ denote, respectively, the file length, its total number of sites, the separation between adjacent sites, and the molecular mean life time on one site. The θ denotes the pore filling factor, that is, the occupation probability of the individual sites. Inserting Eq. 24 into Eq. 6 yields, for the self-diffusivity of the individual molecules within a single file (also known as the self-diffusivity of “the center of mass”),

$$D_{\text{s.f.}} = D_{\text{iso}} \frac{1-\theta}{n}. \quad (25)$$

The factor $1-\theta$ appearing on the right-hand side denotes the probability that a jump attempt leads to a vacant site and may thus be taken as a mean-field approach taking account of mutual molecular impediment. The self-diffusivity is, moreover, seen to decrease with an increase of the number n of sites and, hence, of the file length. Under diffusion limitation, the rate of tracer exchange scales with the ratio between the intrinsic diffusivity and the square file length (as immediately visible by dimension analysis). Thus, under single-file conditions, exchange times scale with the third power of the sorbent sizes, rather than with only their square (see, e.g., Eq. 11) under the conditions of normal diffusion. Under single-file conditions, miniaturization is thus seen to become a particularly important issue for performance enhancement whenever molecular exchange is an issue, as for chemical conversion in microporous catalysts.

By its very nature, single-file confinement leaves the rate of uptake and release unaffected and remains undetectable by their measurement. Effects of single-file diffusion, therefore, become amenable to quantification only by investigating self- or tracer-diffusion.

2.2 Impact of pore space heterogeneity: diffusion in particle assemblies

In most technological applications and in numerous types of diffusion measurement, the nanoporous material occurs in an assemblage of nanoporous sorbents, including pressed pellets and beds of sorbents. In such a case, one may distinguish between concentrations in the macro (meso) pores (i.e., in the space between the individual microporous particles, commonly referred to by c) and in the micropores (space within the adsorbents, referred to by q). It should be noted that the discussion here is limited to a single gaseous component and assumes the validity of the ideal gas law. In this case, on a macroscopic scale, that is, within a pellet or bead, the notation of Fick's 2nd law as introduced with Eq. 4 is now extended to

$$\varepsilon_p \frac{\partial c}{\partial t} + (1 - \varepsilon_p) \frac{\partial \bar{q}}{\partial t} = \frac{\varepsilon_p}{\tau} D_p \frac{\partial^2 c}{\partial X^2} \quad (26)$$

with the parameters ε_p and τ denoting, respectively, the void fraction of the macropores and the effective tortuosity of the pellet. Differing from Eq. 4, there now appear two terms on the left-hand side, taking account of the accumulation in both the macro- and micropore phases. Variation in concentration is balanced by mass transfer through the macropores (right side of Eq. 26). The X denotes the spatial coordinate through the pellet, and D_p stands for the relevant diffusivity in the macropores. The prefactors appearing on the right-hand side take into account that for mass transfer within the macropores only the fraction ε_p of total space is available and that the actual distance traveled has to be corrected by an effective tortuosity of the pellet, τ . This quantity is “derived” from the measured diffusion time by macroscopic measurements when surface diffusion is negligible. This can be achieved by an appropriate choice of the probe molecule and the experimental temperature range if the average pore dimension is determined from mercury intrusion data (see, e.g., Hu *et al.*³⁸). On good-quality commercial materials, the derived value for τ should not be too far from the inverse of the void fraction. Smaller values are an indication of an additional flux from surface diffusion, while significantly larger values may indicate either the intrusion of heat effects or the poor quality of the material. Consistency between techniques that have different contributions, for example, ZLC (molecular and Knudsen) and uptake measurements (Knudsen and viscous flow if pure components are used), ensures the correct definition of the effective average diameter and tortuosity of the formed material (see, e.g., Hu *et al.*³⁸).

Generally, the solution of Eq. 26 necessitates coupling with the mass balance (diffusion equation) in the micropore phase at each position X within the pellet (see, e.g., Section 6.2 in Kärger *et al.*⁶). Thus, the overall uptake or release time becomes a function of both the micro- and macropore diffusivities.

An important limiting case is obtained when the diffusion in the micropores is sufficiently fast so that the micropore concentration can be considered at equilibrium with the local concentration in the macropores and the system becomes macropore-diffusion controlled

$$\frac{\partial c}{\partial t} = \frac{\varepsilon_p}{\tau} \frac{D_p}{\varepsilon_p + (1 - \varepsilon_p) \frac{dq}{dc}} \frac{\partial^2 c}{\partial X^2} = D_{\text{eff}} \frac{\partial^2 c}{\partial X^2}. \quad (27)$$

Equation 27 with X as the spatial coordinate through the pellet is thus seen to assume the form of Eq. 4, with an effective (macropore!) diffusivity appearing as the prefactor on the right-hand side.

It is important to note that, especially when dealing with small particles at micrometer or sub-micrometer scale, it is difficult to disperse particles and avoid agglomeration. Therefore, in the presence of agglomeration, a system may behave as an assemblage of particles and become macropore-diffusion limited.

The transport mechanisms that contribute to D_p are molecular diffusion, Knudsen diffusion, viscous flow, surface diffusion, and micropore diffusion.⁶ The first three mechanisms occur in the macropores of an adsorbent particle. Adsorbent particle size (radius of a spherical particle or equivalent radius of a non-spherical particle) is the characteristic dimension that affects the diffusional time constant.

The molecular diffusivity, D_m , is inversely proportional to the pressure and proportional to some power of the temperature. The D_m can be estimated from well-established semi-empirical equations (e.g., Chapman–Enskog equation). The Knudsen diffusivity, D_K , on the other hand, is independent of pressure and the effective correction in good-quality commercial materials is similar to that for the other contributions. There usually is not enough information in the kinetic responses to distinguish any additional contributions, and this may reflect averaging effects in real systems. Therefore, experiments carried out at constant partial pressures, but different total pressures, can be used to identify molecular diffusion as the dominant contribution, if the measured effective diffusivity is inversely proportional to the pressure.

The Knudsen diffusivity, D_K , is often the dominant contribution for the diffusion of gases in mesopores, when the mean free path exceeds the local pore diameter. It is typically estimated from the following equation, which is valid for infinitely long, smooth, cylindrical pores:

$$D_K = \frac{2}{3} r \sqrt{\frac{8R_g T}{\pi M}}, \quad (28)$$

where r is the pore radius, T is the absolute temperature, R_g is the universal gas constant, and M is the molecular mass of the gas. For “real” systems, Eq. 28 cannot be more than a first approach. Thus, with both experiments and simulation-based approaches, in good-quality commercial beads and pellets, Eq. 28 is often found to require another prefactor, $\frac{9}{13}$, in addition to $\frac{2}{3}$ (Derjaguin’s correction^{39,40}). Additional corrections based on theory may be considered (see Section 4.2), but the information needed to apply such corrections is not always readily available.

When experiments are carried out under variable total pressure conditions flow will give an additional contribution that can be expressed as viscous diffusion

$$D_v = \frac{Pr^2}{8\eta}. \quad (29)$$

This is based on Poiseuille flow in a cylindrical tube, with P referring to the total pressure and η to the viscosity. Viscous flow contributions are usually less important in nanopores but can become the most significant contributor to transport in macropores. It should be noted that this is not a diffusive but a convective contribution, representing transport under a total pressure gradient, rather than a concentration gradient, but these are proportional for a pure, ideal gas under isothermal conditions.

Finally, surface diffusivity (D_s) refers to the contribution to material flux in a pore from transport through a physically adsorbed layer. This can be due to transport in a phase adsorbed on the surface of the macropore or the flux in the micropores along the direction of the macropore as in the biporous model the adsorbent particle is reduced to a point accumulation source/sink in the macropore mass balance (Eq. 26). As such the surface diffusivity is obtained by subtracting all the other contributions or by running experiments at low temperatures where the absorptive is a vapor and surface diffusion can become the dominant contribution, see, for example, Ruthven and Xu.⁴¹

The contribution of surface diffusion to D_p can be expressed as follows:

$$D_{sp} = \frac{1 - \varepsilon_p}{\varepsilon_p} \frac{dq_{eq}}{dc} D_s \quad (30)$$

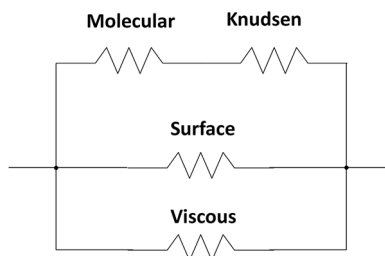


Fig. 2: Electrical analog of resistances to transport in porous materials. Adapted from (Ref. [6]) p. 94 with permission.

with q_{Eq} denoting the concentration in the nanopores in equilibrium with the concentration c in the macropores. At low concentrations $\frac{dq_{\text{Eq}}}{dc}$ reduces to the Henry's law constant, while for self-diffusion and tracer exchange measurements it becomes $\frac{q_{\text{Eq}}}{c}$ as the experiment remains at a constant concentration. Surface diffusion will normally become negligible at temperatures well above the normal boiling point of the adsorbate.⁶

To combine all the contributions into a single pore diffusivity, an equivalent resistor network is used with the inverse of the diffusivity being equivalent to an electrical resistance. In this resistor network, molecular and Knudsen mechanisms correspond to resistances in series (Bosanquet approximation), with the resulting resistance in parallel to those corresponding to surface and viscous mechanisms as shown in Fig. 2.

The overall pore diffusivity is given by the following equation:

$$D_p = \left(\frac{1}{D_m} + \frac{1}{D_K} \right)^{-1} + D_V + D_{\text{sp}}. \quad (31)$$

In the micropores, the adsorbate is always under the adsorption force field of the pore wall. The micropore diffusivity is commonly measured experimentally by fitting an appropriate diffusion model to some measured data. Surface diffusivity and micropore diffusivity may depend on the adsorbed phase concentration in the nonlinear range of an isotherm. Hence, both the initial condition and size of the step perturbation used in the experiment are important for a proper interpretation of the measured diffusivity value. It is customary to report the micropore (and also surface) diffusivity values measured in the linear range of the isotherm, called the limiting diffusivity, D_0 .

3 Measurement techniques

Measurement of the determining parameters of guest diffusion in nanoporous materials is, quite in general, based on the recording of some variation within the system under study which—ideally unambiguously—may be referred to guest diffusion. Corresponding to the existence of a multitude of diffusion-related phenomena, there is also a multitude of experimental techniques for their measurement. In the following, we are going to provide a survey of the most important techniques presently in use for diffusion measurement in nanoporous materials. Given the rapid development in the field, with an ever-growing diversity in the systems considered and, correspondingly, in the challenges in their investigation, this compilation cannot claim to be exhaustive. It does, however, strive to refer to the most important principles of measurement as resulting from the presentation of diffusion fundamentals in Section 2 and to introduce some of the routes presently in use for their experimental realization.

3.1 General considerations for batch uptake measurements

While each technique for experimentally exploring diffusion in nanoporous materials will have specific requirements, there are some general considerations that apply to all batch uptake approaches, namely, gravimetric, volumetric, and frequency response techniques (Sections 3.3 and 3.6) in closed systems. They should,

correspondingly, also be taken account of in the application of (notably X-ray computed and NMR) imaging techniques (Sections 3.9 and 3.10).

As adsorption is associated with a phase change, there will always be a temperature variation associated with an uptake measurement. To limit such effects, it is important to reduce the pressure steps as much as possible. A balance has to be struck in order to have a good signal-to-noise ratio, which should correspond to the largest step that provides a linear response, that is, the dimensionless response is independent of the pressure step used. For fast diffusing systems, even in the case of a linear response, it is not possible^{42,43} to eliminate heat effects and the interpretation of the experiments will require the use of models that include combined mass and heat transfer relationships. In this case, independent measurements of adsorption isotherms should be used to determine the adsorption energies in order to limit the number of physical parameters needed to interpret the dynamic responses. To confirm experimentally that heat effects can or cannot be neglected, the samples used should be dispersed as finely as possible and repeat experiments with inert metal materials added should be performed. The addition of metal beads will result in a change in the dimensionless groups present in the non-isothermal models, thus providing additional data to arrive at improved estimates of the diffusion coefficients.

For the case of a type I (i.e., Langmuir-type⁴) isotherm, the diffusivity will increase significantly with concentration, either by the thermodynamic correction (micropore diffusion, Eq. 23) or the denominator in the effective diffusivity (macropore diffusion, Eq. 27), and as a result heat effects will become dominant in fast diffusing, strongly adsorbed components at high adsorbed phase concentrations. In this case, experiments should be performed at the lowest pressure possible, followed by experiments at higher pressures.

When the samples are made of fine particles agglomeration can occur. This leads to the possibility that the response of the experiment is affected by the way in which the sample is configured, and this is typically referred to as a “bed effect,” resulting in an apparent effective diffusivity that is similar to macropore diffusion control. It is therefore important to ensure fine dispersion of the particles. This applies also to studies on formed materials. Experiments are hence ideally performed with different sample masses to ensure that the system is not affected by bed effects. Dispersion of the solid for powders can be achieved using rock or glass wool, while for beads and pellets special sample holders can be manufactured that isolate the beads and pellets.

To avoid both bed and heat effects, small sample masses should be used in uptake experiments. For strongly adsorbed components, practical ranges are below 50 mg. For weakly adsorbed components, larger masses can be used. In any case, the experimental checks outlined above should be performed.

As the conditions in which the experiments are performed determine which model should be used in the interpretation of the results, the general workflow is similar for all batch uptake experiments. Fig. 3 provides a summary of the recommendations for batch uptake experiments as well as an indication of which model should be applied. The key points are that the experiments should verify the main assumptions in the models used and that both adsorption and desorption experiments should be performed. For adsorption isotherms that do not show a hysteresis loop, performing both adsorption and desorption experiments is also a very useful means to detect leaks, which would appear as an apparent open hysteresis in volumetric and gravimetric/volumetric systems. “Frequency response” experiments are by definition adsorption/desorption experiments.

3.2 General considerations for flow measurements

In flow systems typically, an inert carrier gas is present and in general the conditions will be closer to isothermal compared to batch experiments. Again, some general considerations apply to all flow systems, namely: flow frequency response (Section 3.6), breakthrough and chromatographic experiments (including tomography measurements, Sections 3.5, 3.9, and 3.10) in flow gravimetric systems, and zero length column experiments (Section 3.4).

To ensure near-isothermal conditions, small sample masses should be used and the material should be packed in small diameter pipes. This in turn requires the need to minimize dead volumes in the system, which should in any case be quantified using blank response experiments, that is, experiments without any adsorbent material. If thermal effects cannot be avoided, the system should include temperature measurements, ideally in at

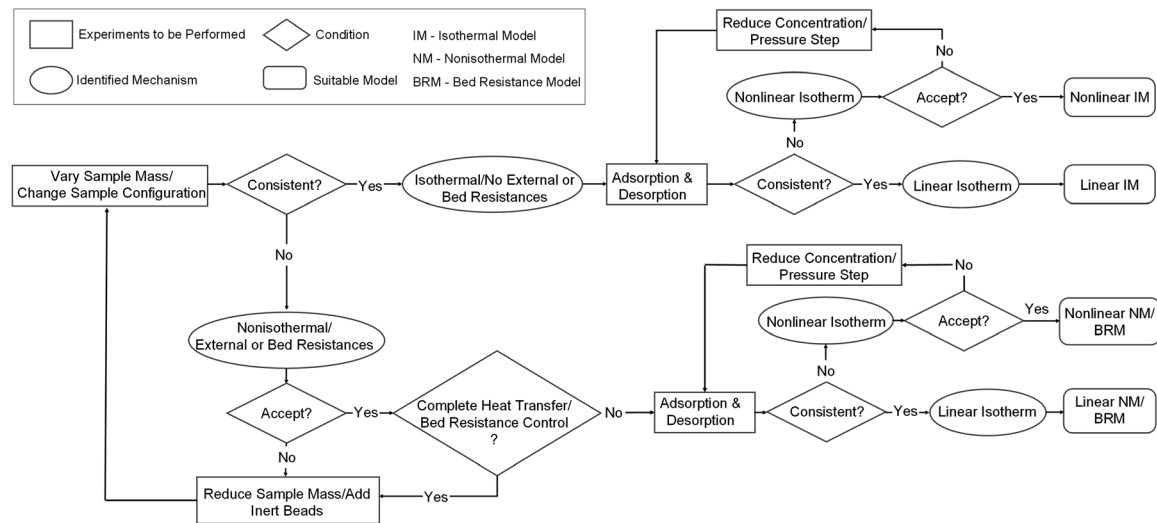


Fig. 3: Schematic workflow of experiments and decisions that lead to the use of the appropriate model to match adsorption kinetics in batch uptake experiments. Adapted from Wang *et al.*⁴⁴ with permission.

least two locations along the column, as this allows to determine the velocity of the thermal fronts, providing data that can be used to quantify the thermal parameters of the model.

Small concentration steps will reduce thermal effects due to the presence of the inert carrier gas. Therefore, in flow systems as the concentration steps are reduced the system will become isothermal, and whether this can be achieved is a matter of the sensitivity of the composition detector used.

When using powders, pressure drops along the column may become large. It is preferable to reduce the length of the column, but if this is not possible the model used for the interpretation of the results should include an appropriate pressure drop correlation and the pressure at the column inlet should be recorded to ensure that the correlation used is accurate.

While the presence of the carrier gas helps reduce thermal effects, it also introduces bulk gas diffusion as an additional mass-transfer resistance. It is therefore very important to perform experiments with different carrier gases to confirm the nature of the main mass-transfer mechanism. Unless the dimension of the adsorbate molecule is very close to one of the dimensions along the diffusion path, typically macropore diffusion will be the controlling mechanism if pores larger than the nanoporous range are present. Macropore diffusion control can also occur when using small particles due to agglomeration. Note that a change in the carrier gas as well modifies the external heat transfer coefficient, providing a useful check on also the assumption of isothermal conditions.

All flow systems can operate under equilibrium control. This is achieved when the rate at which the external gas concentration is changing is slower than the internal diffusion process. Therefore, the adsorbed phase concentration is always at equilibrium with the fluid phase and diffusion measurements are not possible. It is essential to perform experiments at different flowrates in order to exclude equilibrium control. For very short columns, experiments at different flowrates will overlap when plotted versus the product of the volumetric flowrate and time. For long columns in equilibrium control, the dispersion relative to the mean residence time will decrease with the increasing flowrate as a result of the effect of axial dispersion. The dispersion will reach a minimum and then increase as a result of the effect of internal mass-transfer resistances. Diffusion measurements must be performed in the region where the dispersion relative to the mean residence time increases with flowrate, where the system is sufficiently far from equilibrium control.

If the response of the system is not linear, it is essential to perform both adsorption and desorption experiments. The frequency response technique does this by default. Pulse or chromatographic experiments also provide this directly. To understand the importance of this point one can consider the case of a type I (i.e., Langmuir-type⁴) isotherm and the response of an isothermal breakthrough column for a single adsorbate. In

adsorption, the concentration front will self-sharpen as equilibrium theory predicts that the response will be a shock front. In desorption, the front will self-broaden. Therefore, desorption will contain the information on the shape of the isotherm, and the combination of adsorption and desorption will allow to determine both equilibrium and kinetic parameters unambiguously. It is possible to measure independently the adsorption isotherm, but it is always necessary to check that the predicted mean residence time matches exactly the observed value, otherwise the estimated diffusion coefficient will be affected by this deviation in an attempt to compensate for the error in the equilibrium value. If the isotherm parameters are measured independently, the determination of the diffusion coefficients should be performed relative to the mean residence time.

From the considerations above, it is clear that ideally flow experiments should be performed under linear conditions (small concentration steps) with small sample masses (to ensure near-isothermal conditions). Under these conditions, initial estimates of the diffusion coefficients can be obtained using the moments of the responses combined into the “height equivalent to a theoretical plate” (HETP, symbol H) to obtain a Van Deemter plot (HETP versus flowrate or fluid velocity⁴⁵). This approach produces the total dispersion relative to the mean residence time and allows to check that the HETP increases with flowrate, confirming that the system is not equilibrium controlled. To quantify axial dispersion and the overall mass-transfer resistance, at least 3 flowrates are needed. It is important to stress that this approach is only valid for linear isothermal systems and both adsorption and desorption experiments must be performed to confirm the validity of these assumptions.

The first and second moments, μ and σ^2 , respectively, in an adsorption column for a pulse or chromatographic experiment are obtained from

$$\mu = \frac{\int_0^\infty ct dt}{\int_0^\infty c dt} \quad \sigma^2 = \frac{\int_0^\infty c(t - \mu)^2 dt}{\int_0^\infty c dt} \quad (32)$$

with c denoting the outlet concentration at time t , while for a step or breakthrough experiment, they are obtained from

$$\mu = \int_0^\infty \left(1 - \frac{c}{c_0}\right) dt \quad \sigma^2 = 2 \int_0^\infty \left(1 - \frac{c}{c_0}\right) t dt - \mu^2, \quad (33)$$

where c_0 stands for the initial value of c . The HETP (H) is defined as

$$\frac{H}{L_c} = \frac{\sigma^2}{\mu^2}, \quad (34)$$

where L_c is the length of the packed section of the column. Haynes and Sarma⁴⁶ obtained the expressions for the first and second moments in terms of the different contributions to mass transport in an adsorption column. These are also reproduced in several reference sources, see, for example, Ruthven⁴⁵ and Kärger et al.⁶ that also include corrections for cases where pressure drops are significant.

In all the expressions needed to obtain the moments from the experimental signals, it is necessary to calculate integrals over an infinite time. In practice though this is not necessary as all dynamic responses of adsorption columns will eventually become an exponential decay. If this long-time asymptote is identifiable, then the integrals in Eqs. 32 and 33 should be calculated numerically up to the point where the signal reduces to an exponential decay, followed by an analytical determination of the integrals of the tail (see, e.g., Brandani and Ruthven⁴⁷). Note that this approach significantly reduces the effect of signal noise on the calculation of the HETP when compared to direct integration of the raw signal, as the effect of the noise increases dramatically with time for the higher moments.⁴⁸

3.3 Uptake and release measurements

Uptake experiments are generally carried out introducing a change in the external adsorptive concentration and monitoring the sample mass (gravimetric) or the pressure of the system in a fixed volume (volumetric or

piezometric). Both types of experiments measure transport diffusivity (Fig. 1a) if a known narrow range of sorbent sizes is used. In the case of gravimetric measurements, tracer exchange with isotopes of the adsorbates can be carried out^{49,50} (Fig. 1b), but these measurements are rare. Most uptake experiments are performed using a single adsorbate, and the discussion here will be limited to this case.

Gravimetric systems differ primarily in terms of how the external concentration is changed and if the balance is symmetric or asymmetric.⁴⁴ There are three main modes by which the concentration of the adsorbate is changed: A) a flow controller is combined with a back-pressure regulator and the pressure is gradually increased to a new setpoint; B) a step in inlet concentration is generated in a system at constant pressure using a carrier gas; C) a large volume is equilibrated at a new pressure and a valve is opened to introduce or remove the adsorbate from the volume where the balance is present.

System (A) allows to set the final equilibrium pressure, but pressure changes are often smoothed over a period of at least a minute to avoid oscillations in the balance.

Balances (B), where the adsorbate is introduced in flow diluted in a carrier gas, are closely related to the zero length column (ZLC) system discussed in Section 3.4, with the main difference being that the measured quantity is the adsorbed amount. All instructions given for the ZLC will apply for these systems and in particular changing the carrier gas from argon (typically used in thermo-gravimetric analysis systems) to helium should be an essential requirement for kinetic measurements.

System (C) is effectively a gravimetric-volumetric system, and if the total pressure change is not-negligible the models of the volumetric experiment should be used.

As commercial systems are often designed for the accurate measurement of adsorption equilibrium, including protections that avoid strong oscillations, reliable results are limited to relatively slow systems with diffusion times (Eq. 13) of the order of a few minutes or above. The investigation of systems with shorter diffusion times on a balance thus requires a most careful interpretation of the dynamics of the specific model to correct for blank effects. This requirement becomes increasingly complex for high pressure measurements where buoyancy corrections (and possibly drag effects) are important and cannot be subtracted based on final equilibrium values.

Almost all volumetric systems (see schematic diagram in Fig. 4) measure the pressure of the gas in the dosing cell. Through a mass balance, Eq. 35, the amount adsorbed at time t , ($V_s \bar{q}(t)$), is obtained as.

$$V_d c_d(t) + V_u c_u(t) + V_s \bar{q}(t) - V_d c_d(0) - V_u c_u(0) - V_s \bar{q}(0) = 0 \quad (35)$$

with c denoting the concentrations in the gas phase and $\bar{q}$ the average concentration in the adsorbed phase of volume V_s .

Often the ideal gas state is assumed, $c = \frac{p}{R_g T}$, but at low temperatures and high pressures an accurate equation of state is needed to convert pressure data to gas phase concentrations^{51,52} and proper account must be given to the presence of different temperature zones in the apparatus.

As fast acting valves are available it is in principle possible to measure fast diffusing systems with a volumetric apparatus, but often commercial units are limited by data acquisition rates below 1 Hz or by the presence of filters in the lines that limit the rate of gas flow when the valve is opened. For fast systems, it becomes important to take into account the flow of gas in the system and this can be achieved using a model that includes a finite valve conductance,⁵³ leading to the ability to measure diffusion times greater than 0.5 s.

Under isothermal and linear conditions, the solution to diffusion in a sphere with the radius R subject to an instantaneous step change gives the dimensionless uptake in Eq. 36

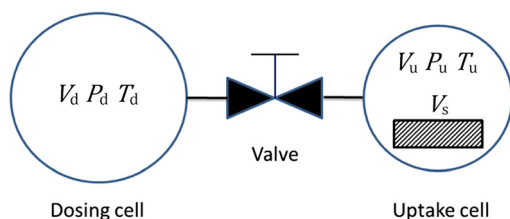


Fig. 4: Schematic representation of a volumetric system, comprising the dosing (subscript d) and uptake (subscript u) cells and the volume of the solid V_s . Adapted from (Ref. 44) with permission.

$$\frac{m_t - m_0}{m_\infty - m_0} = \frac{\bar{q}}{q_\infty} = 1 - \frac{6}{\pi^2} \sum_n \frac{\exp\left(-n^2 \pi^2 \frac{D_T}{R^2} t\right)}{n^2} \quad (36)$$

with $m_{t(0,\infty)}$ denoting the adsorbent mass at time t , 0, and ∞ . $\bar{q}$ and q_∞ stand for the mean adsorbate concentration and its final (equilibrium) value, respectively.

Often uptake data are plotted vs. $\sqrt{t}$ given that for short times

$$\frac{\bar{q}}{q_\infty} \approx 6 \sqrt{\frac{D_T}{R^2}} \frac{t}{\pi} - 3 \frac{D_T}{R^2} t + \dots, \quad (37)$$

but the first term approximates Eq. 36 only for $\frac{\bar{q}}{q_\infty} < 0.2$. Therefore, it is recommended that the full solution is always used to compare the experimental results and the model.

Equation 36 can be used in gravimetric systems when the response of the blank is at least an order of magnitude faster than $\frac{R^2}{D_T}$ (the diffusion time). It should never be used for volumetric systems where the varying pressure is the measured quantity as this solution is based on the assumption that the gas phase pressure remains constant.

For volumetric systems, it is preferable to use directly the measured pressure in the dosing cell and plot the dimensionless pressure, σ_d ,⁵⁴ vs. the solution to the diffusion model including the valve effect for an ideal gas

$$\sigma_d = \frac{P_d - P_\infty}{P_d^0 - P_\infty} = \sum_{n=1}^{\infty} \left[a_n \exp\left(-\beta_n^2 \frac{D_T}{R^2} t\right) \right] \quad (38)$$

with

$$a_n = \frac{1 + 3\delta + 3\gamma}{1 + 3\gamma} \frac{2\omega^2 \delta \beta_n^2}{2\omega^2 \delta \beta_n^2 + (\omega - \beta_n^2)^2 (\beta_n^2 + z_n^2 - z_n + 2\gamma \beta_n^2)} \beta_n \cot \beta_n - z_n = 0$$

$$z_n = 1 + \gamma \beta_n^2 + \frac{\omega \delta \beta_n^2}{\omega - \beta_n^2} \quad \gamma = \frac{1}{3R_g T_u} \frac{(P_\infty - P_u^0) V_u}{(q_\infty - q_0) V_s} \quad \delta = \frac{1}{3R_g T_d} \frac{(P_\infty - P_u^0) V_d}{(q_\infty - q_0) V_s} \quad \omega = \frac{R_g T_d}{V_d} \frac{\bar{\chi} R^2}{D_T}.$$

The parameter $\bar{\chi}$ is a valve constant with the dimension $\text{mol s}^{-1} \text{Pa}^{-1}$. Subscripts d, u, and s denote dosing, uptake, and solid, respectively. The dimensionless pressure avoids the confusion in defining the uptake from the measured pressure for short times⁴⁴ and allows to distinguish between diffusion and surface barrier kinetics.^{54,55}

The most common issue with uptake measurements is the presence of heat effects. This is particularly true for fast diffusing systems (diffusion times below 1 min). For type I (i.e., Langmuir-type⁴) isotherms, the problem increases with pressure as the diffusivity increases rapidly while the heat transfer parameters have only a minor concentration dependence. Furthermore, reducing the size of the pressure step can be used to confirm linearity but not to exclude heat effects.^{42,56,57} The analytical solutions in this case have a structure similar to Eq. 36 and⁴⁴ therefore it is very difficult to separate heat and mass-transfer contributions unless a wide range of experiments are performed and the configuration of the solid is modified. At least experiments with inert metal added to the solid should be performed to determine if the system is heat limited. If heat limitations are not avoidable, accurate adsorption isotherms at several temperatures should be measured to accurately characterize the heats of adsorption and minimize the parameters to be determined from the kinetic experiments.

There is a tendency to use large sample sizes to improve the accuracy of the experimental results.⁴⁴ While this can be advantageous for equilibrium measurements, kinetic measurements should be performed with as little material as possible. To increase the sensitivity of gravimetric systems, the balance should be in a basement or ground floor.

3.4 Zero-length column (ZLC)

The ZLC technique was introduced by Eic and Ruthven⁵⁸ with the aim of overcoming the difficulty of measuring adsorption of fast-diffusing and strongly adsorbed molecules in zeolites and other microporous materials. It consists of a small sample placed in a flow system where the inlet concentration can be varied, typically between a pure inert carrier and a mixture of the carrier and the molecule of interest. The sample is allowed to reach equilibrium with the mixture. Then the flow is switched to pure carrier and desorption is monitored. The key advantages are near-isothermal conditions and the simple analysis required as the system dynamics are those of a well-mixed unit. The technique can be used to measure transport diffusivity (Fig. 1a) or tracer exchange⁵⁹ at varying concentrations (Fig. 1b) using, for example, deuterated and hydrogen forms of the same molecule.

The signal-to-noise ratio of most detectors is much better in desorption and as a result the transport diffusivity at zero loading is measured in the vast majority of cases. A well-designed system can be used to measure diffusion times of 1 to 2 s, while most systems can provide accurate measurements with diffusion times larger than 30 s. The range of measurable diffusivities depends on the dimension of the particles with the longest observation times so far reported of up to 20 h. A clear advantage of the ZLC over other flow systems is the fact that the pressure drop is negligible even with very small particles.

Assuming that the concentrations are sufficiently low to be in the Henry's law region, that is, linear equilibrium, and a constant diffusivity D_T in a spherical sorbent particle of radius R , the solution to the coupled column mass balance and diffusion equation can be represented by⁶⁰

$$\frac{c}{c_0} = \sum_n \frac{2L \exp\left(-\beta_n^2 \frac{D_T}{R^2} t\right)}{\beta_n^2 + (\gamma\beta_n^2 + 1 - L)^2 + \gamma\beta_n^2 + L - 1} = \sum_n a_n \exp\left(-\beta_n^2 \frac{D_T}{R^2} t\right) \quad (39)$$

$$\beta_n \cot \beta_n + L - 1 - \gamma\beta_n^2 = 0, \quad (40)$$

where

$$\gamma = \frac{1}{3} \frac{V_F}{KV_S}, \quad L = \frac{1}{3} \frac{F}{KV_S} \frac{R^2}{D_T}. \quad (41)$$

Here F is the flowrate of the carrier, V_F is the volume of the fluid phase, and V_S is the volume of the solid. These two dimensionless groups are key to understanding the response of a ZLC. The parameter γ is the ratio between the total amount of molecules in the fluid and the adsorbed phase, with K the Henry's law constant (limiting slope of the adsorption isotherm). The parameter L represents the ratio of the diffusion time, R^2/D_T , and the washout time constant of the adsorbed phase. This parameter governs whether mass transport can be measured. Small values of L , fast diffusion, large sample size, and low flowrates indicate that the external concentration is varied too slowly to generate an internal concentration profile. Under these conditions, $L < 1$, the ZLC can be used to measure equilibrium, which can be useful when investigating the concentration dependence of the diffusivity. For large values of L the system becomes mass transfer limited, but if L is too high the signal drops very rapidly to values near zero. Therefore, the best results are generally achieved when $10 < L < 100$. This guides the design of the ZLC, setting the range of gas flowrates as well as the sample size. In most cases, a union fitting is used to house the sample and masses in the range 0.5–10 mg are typically used. The lower range applies to very strongly adsorbed molecules, and the larger value is used for more weakly adsorbed species. Note that the ZLC can also be used to measure mass transfer in single beads or pellets.

For $\gamma < 0.01$, that is, for strongly adsorbed components, Eq. 39 will depend only on L and the diffusion time and the structure of Eq. 39 shows that there is a long-time exponential decay corresponding to the smallest root of Eq. 40, β_1 . The intercept of the asymptote can be used to determine L and hence β_1 , allowing a first estimate of the diffusion time from the slope of the asymptote. This method should be used only as a way to obtain a first estimate as the intercept will be affected strongly by isotherm nonlinearity and the selection of the actual asymptote can depend on the time interval of observation.⁶¹ To arrive at a robust estimate of the diffusion time, it is necessary to

perform experiments at least at two different flowrates (vary L which should be proportional to the flowrate) and also perform a partial loading (PL) experiment. This is achieved by switching to adsorption only for a short time (less than one tenth of the diffusion time) and rapidly switching back to the pure carrier without allowing the system to equilibrate. The PL experiment requires a fast-acting valve (or system of valves) and an accurate pressure balance between the carrier and mixture gas lines. Performing PL experiments provides us with the time t_s between valve switches as an additional free parameter. Because of the differences in the resulting internal concentration profiles, most importantly, variation of t_s allows to discriminate between limitation by diffusion and surface barriers.

The recent review of 30 years of ZLC practice⁶¹ discusses in detail the problems that can be encountered if experimental checks or the background theory are not well understood. Any user of the technique should consult this more extensive account, as it is important to learn from practical examples like in Fig. 5.

To ensure that the ZLC responses are interpreted correctly, one should perform the following checks:

- (1) Run experiments with different carrier gases. Essential to distinguish micropore and macropore diffusion control, including when particle agglomeration is suspected.
- (2) Experimental conditions should be adjusted to achieve values of the L parameter between 10 and 50, also varying the sample mass to confirm zero-length behavior.

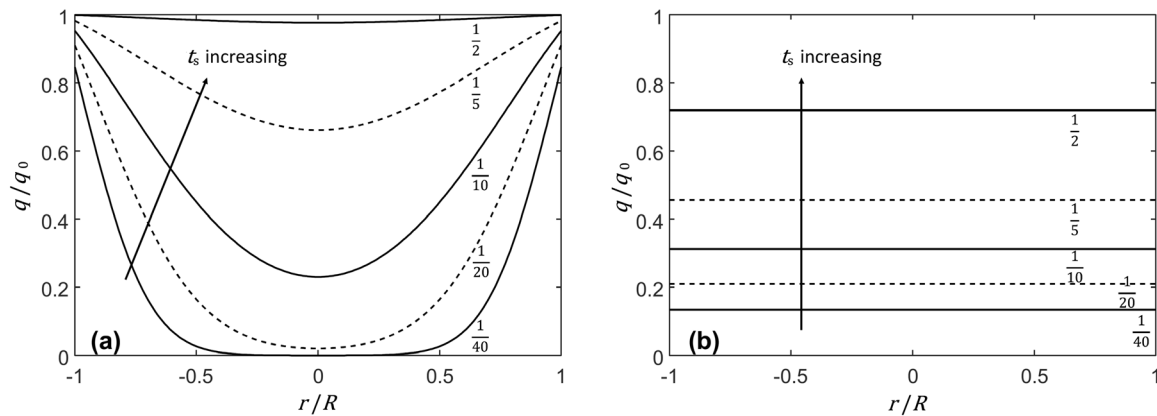


Fig. 5: Internal adsorbed phase concentration profiles at different t_s/D values. (a) Diffusion. (b) Surface barrier. $L = 20$ and $\gamma = 0.05$. Plots show the relative concentration $\frac{q}{q_0}$ as a function of the spatial coordinate r divided by the particle radius R . Adapted from Brandani and Mangano (Ref. 61) with permission.

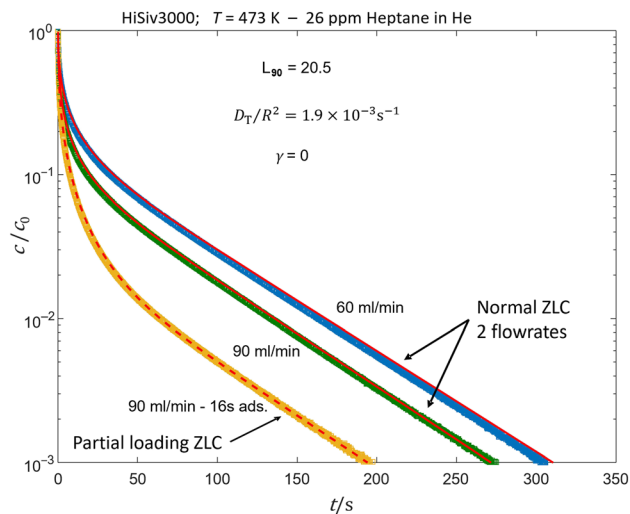


Fig. 6: Full model simultaneously fit to single-pellet experiments at two flowrates and one partial loading. The parameter L and the diffusion time R^2/D_T are explained below Eq. 41.

- (3) Curves at different flowrates (at least 2), and partial loading experiments should be used to identify unambiguously the kinetic time constant.
- (4) A concentration-vs- Ft (product of the volumetric flowrate and time, or eluted volume) plot should be included to show that the responses are in the kinetic regime and are consistent.⁶² The blank responses should be shown on this plot to confirm that there is sufficient information to analyze the curves, particularly for weakly adsorbed components.
- (5) Check for linearity by performing experiments at different initial concentrations.

In the analysis of the results, the following rules apply:

- (1) The full model solution should be compared to the experimental data with a single set of model parameters (see Fig. 6) as this will confirm consistency of the results and identify clearly when more complex models (e.g., combined diffusion and surface resistance) may be required.
- (2) If system linearity is not achieved either by design⁶³ or because the signal becomes too noisy, low flowrate experiments should be performed to correlate independently the equilibrium isotherm.
- (3) If the model includes a distribution of particle sizes, data using different adsorbates should confirm that the results are consistent.
- (4) Especially for weakly adsorbed components, a detailed blank deconvolution should be used⁶⁴ or alternatively a model of the blank should be combined to the dynamic response of the ZLC.

Finally, when reporting the results, the diffusion times (Eq. 13) should be included along with the dimension used to obtain the diffusivity. Ideally, adsorbents with a narrow size distribution should be used and experiments with two different average sizes, where possible, should be presented to confirm diffusion control. Note that when studying pellets or other formed materials it is preferable to use, for such checks, fragments of the original pellet and/or vary the carrier gas rather than use pellets of significantly different sizes, which could have different tortuosities and binder content.

3.5 Adsorption column dynamics

3.5.1 Measuring arrangement and principle

In this section, we refer to measurements of the gas phase concentration at the exit of a column packed with an adsorbent. Alternatively, one can also consider measuring the evolution of the guest distribution in the adsorbed phase, for example, using X-ray Computed Tomography Imaging (Section 3.9) or NMR Imaging (Section 3.10). Measuring arrangements and special cases considered in this section are thus of more general relevance.

The response of an adsorption column to either a pulse or step adsorbate concentration perturbation at the inlet can be effectively used to obtain equilibrium and kinetic data. The response to a step perturbation is also known as a dynamic column breakthrough curve, DCB in short.

To obtain a diffusion coefficient from column dynamics, a multiscale model is used. In a typical configuration of a column packed with beads, the model will include the mass balance in a biporous particle, Eq. 26, coupled with the mass balance along the main dimension of the column. This introduces the need to quantify axial dispersion. If the pressure in the column changes due to the flow, an additional pressure-drop equation is needed. If the system is not isothermal, an energy balance has to be added to describe the temperature change along the column. By comparison, a ZLC system is sufficiently short so that the pressure drop can be neglected; in the limit of zero length the mass balance becomes that of a perfectly mixed cell avoiding the need to quantify axial dispersion; and conditions are set so that the system remains isothermal under most operating conditions. The added complexity of a DCB can be justified for weakly adsorbed components, where the ZLC response would be too close to a blank.

The DCB response is matched to the model predictions until a suitable set of parameters is determined by nonlinear regression, typically after some of the parameters in the model are estimated from known correlations.

It is not possible to isolate the contribution of diffusion in nanoporous materials unless this is the main controlling mechanism. As a result, uncertainties in estimating other contributions will affect the value obtained for the diffusivity.

An alternative to the full model fit of the dynamic response is based on converting the experimental responses at different flowrates to HETP (Eq. 34) values, resulting in simple graphical procedures that allow to determine the axial dispersion and the overall internal mass-transport contribution. Note though that these are strictly limited to small pressure steps where the isotherm can be linearized and isothermal operation is achieved. They are typically applicable also to pulse experiments, if the results are shown to be independent of the amount of adsorbate in the pulse. The simplicity of the analysis will lose some of the information contained in the full dataset, so it would be important to generate full model solutions from the values obtained to confirm the validity of the results. Conversely, the Van Deemter plot (HETP versus feed velocity plot) allows to confirm that the experiments are conducted in the mass transfer-controlled regime and should be used to at least check qualitatively that the dispersion is increasing with increasing flowrate.

The residence time of a DCB contains equilibrium information, and the spread of the response relative to the mean residence time contains kinetic information. Both are affected by the dead volume of the apparatus. Hence, the apparatus should be properly designed to minimize dead volume before and after the column, and the measured response should be corrected for the remaining dead volume, using, for example, the point-by-point method described by Wilkins et al.⁶⁵ The corrected breakthrough responses may then be analyzed to extract adsorption equilibrium (data or isotherm model parameters, provided that both adsorption and desorption experiments are performed) and mass-transfer rate constants. If multiple carefully designed experiments are carried out, it may be possible to identify the transport mechanism. A DCB experiment may be easily extended to measure mixture equilibrium. The DCB responses are affected by axial dispersion and heat transfer characteristics and if these are not known *a priori* careful analysis of the experimental results is required, including measurements with different sorbate molecules to confirm the accuracy of the axial dispersion coefficients.⁴⁵

The schematic of a representative breakthrough apparatus is shown in Fig. 7. For a pulse experiment, a rotary valve is typically present that allows to feed the pulse contained in a short loop. The key elements are as follows: 1. Mass flow controllers (MFCs) that allow for precise control of the flow and composition; 2. the adsorption column is packed with a suitable adsorbent immersed in a water bath; 3. an outlet mass flow meter (MFM); and composition detector, for example, a mass spectrometer (MS). For experiments carried out at atmospheric pressure, the back pressure regulator is not needed and if an inert gas is present the outlet MFM may also be removed as the flowrate can be related to the gas phase concentration.^{66,67} This may be advantageous especially in

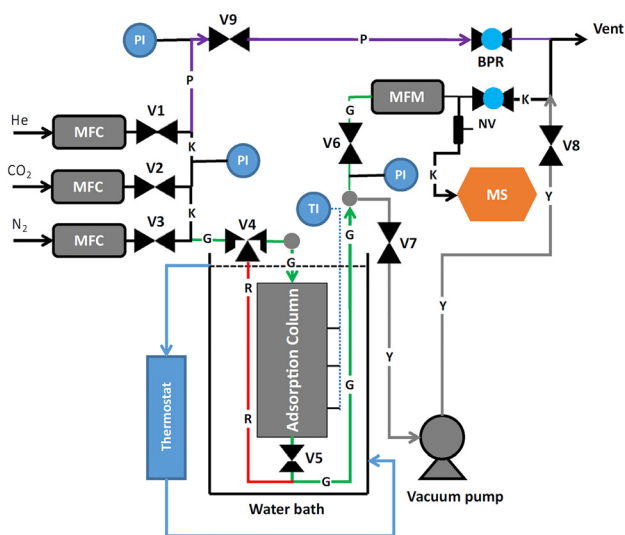


Fig. 7: Schematic of a typical dynamic column breakthrough (DCB) setup. MFC: flow controller; MFM: flow meter; MS: mass spectrometer/gas chromatograph/effluent analyzer; NV: needle valve; PI and TI: indicators of pressure and temperature, respectively; V1–9: valves. Black lines (K): common; green lines (G): measurement of column response including extra-column volume; red line (R): bypass lines for measurement of extra-column volume; purple line (P): flow stabilization; gray line (Y): for column regeneration. Adapted from Wilkins et al.⁶⁵ with permission.

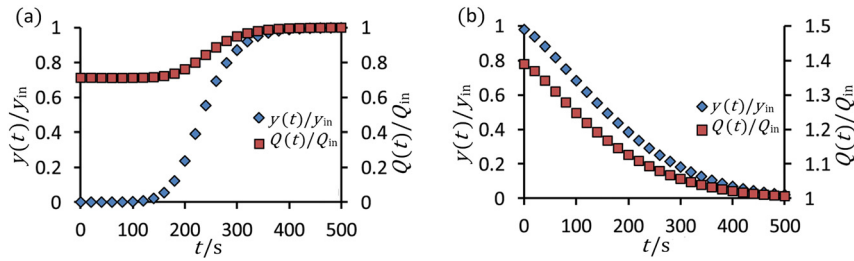


Fig. 8: Typical breakthrough curves for (a) adsorption and (b) desorption experiments. The $Q(t)$ and $y(t)$ are the changing total flow rate and mole fraction at the exit of the adsorber, respectively, which are normalized using the inlet conditions, Q_{in} and y_{in} . Adapted from (Ref. 65) with permission.

systems with small columns, as the back pressure regulator may generate feedback to the MFCs and flow oscillations may occur.

Breakthrough experiments are carried out in adsorption and desorption modes. In an adsorption experiment, the column is initially saturated with either an inert gas, for example, helium, or a gas mixture of known composition. At time $t = 0$, a stepwise increase in the composition of the test gas is introduced and maintained until the experiment is completed. During the entire duration, the composition and flow rate at the column outlet are measured. A typical measurement is shown in Fig. 8 (a). The desorption experiment is performed in the opposite manner, that is, the composition of the test gas is decreased compared to the initial value. Fig. 8 (b) shows the measurements from a desorption experiment. For a complete description of the experimental apparatus and experimental procedures, the readers are referred to the literature.⁶⁵

3.5.2 Adsorption kinetics from breakthrough experiments

The linear driving force model

The linear driving force (LDF) is a common approach to simplify the model for a DCB, based on lumping the overall mass-transfer kinetics into a single time constant. In this approach, the lumped parameter, the LDF coefficient, k , is related to the various resistances by the following equation.

$$\frac{1}{k} = \frac{R_p [\varepsilon_p + (1 - \varepsilon_p)K]}{3k_f} + \frac{R_p^2 \tau [\varepsilon_p + (1 - \varepsilon_p)K]}{15\varepsilon_p D_p} + \frac{R^2}{15D_0}, \quad (42)$$

where k_f represents the external film resistance in the fluid phase. The quantity R_p stands for the radius of the conglomerated particle (bead). Haynes and Sarma⁶⁸ derived the above equation using a moment analysis of the pulse response from a chromatographic column model for linear adsorption equilibrium and three transport resistances in series: external film, macropore, and micropore resistances. This linear additivity rule has been widely used in the literature beyond Henry's law region by replacing $[\varepsilon_p + (1 - \varepsilon_p)K]$ with $\frac{q_{in,E}}{c_{in}}$ ⁶⁹, the slope of the chord of the equilibrium isotherm joining the origin to the equilibrium point corresponding to the feed concentration. In a numerical simulation, it is also possible to define $[\varepsilon_p + (1 - \varepsilon_p)K]$ as the local slope⁷⁰ of the adsorption isotherm, $\frac{dq_E}{dc}$, where q_E is the equilibrium adsorbed phase concentration, making the LDF coefficient concentration dependent. In this case, D_0 should be replaced by D_T .

Therefore, the estimated LDF coefficient is dependent on the quality of the equilibrium data and the goodness of the fitted isotherm model. Note that the LDF approach is only an approximation and if the dominant mechanism for mass transport is a diffusion process the model of the DCB should include the mass balance in the nanoporous material with the appropriate diffusion coefficient, including its concentration and temperature dependence when nonlinear and non-isothermal experiments are analyzed.

Modeling and simulation of breakthrough experiments

Quantitative estimation of kinetic information from DCB experiments requires the solution of a set of equations often collectively called "column dynamics equations." These equations, tabulated elsewhere,⁶⁵ represent the

transport of mass and heat across the column, along with suitable descriptions of pressure drop and the adsorption isotherm. For pulse experiment, only the inlet concentration as a function of time has to be included in the model. The system of equations contains several physical parameters, some of which should be predicted from known correlations. A discussion along with the relevant correlations is included in Wilkins *et al.*⁶⁵ The heat transfer coefficient between the packed bed and the wall is commonly obtained by fitting the temperature responses at various locations along the column. Simultaneous fits of the DCB and temperature profiles should be provided.⁷¹

Estimation and impact of axial dispersion and external film resistances

In general, the contribution of external film resistance is negligible in gas DCB studies, but axial dispersion must be properly accounted for if the objective is to extract intra-particle mass-transport information. Available correlations provide good estimates of the axial dispersion coefficient,⁷² and the complete estimation procedure is detailed in Wilkins *et al.*⁶⁵ Particular care is needed when using very small particles that tend to agglomerate and with strongly nonlinear isotherms where axial dispersion begins to dominate over other resistances. In these cases, and also to verify the axial dispersion predictions, it is better to perform experiments at multiple flowrates in the low flowrate region (see discussion of the Van Deemter plot above), using different carrier gases.^{6,45}

Transport parameters from analysis of DCB responses

By using an independently established equilibrium isotherm model, the LDF constant may be obtained by fitting the measured DCB response if the DCB curve and the model are both normalized using the mean residence time. The corresponding diffusivity values may then be established from further analysis of the LDF constant.⁷³ For a diffusion-controlled system, a pore diffusion model (instead of the LDF model) is preferred to extract the diffusivity. The reliability of the extracted limiting diffusivity value and its concentration dependence may also be simultaneously verified by comparing DCB runs with large concentration step changes with the model predictions including appropriate models for concentration and temperature dependence of the diffusivity.⁷⁴

There is a misconception that in a micropore-controlled adsorbent, breakthrough experiments cannot distinguish between barrier resistance confined at the pore mouth and pore diffusional resistance distributed in the micropore interior. In fact, extent of agreement between the DCBs from pore diffusion and LDF (mathematically equivalent to barrier resistance at the pore mouth) models for a linear isotherm depends on the product

of two parameters, resulting in $\left[\frac{(1-\epsilon_p)K}{\epsilon_p} \frac{DL}{R^2 v_{in}} \right]$ ⁷⁵. It has been experimentally confirmed that it is also possible to

clearly distinguish between the two mechanisms by appropriately choosing of operating conditions using the criterion, and this can also be used to check when the use of the LDF approximation is not sufficiently accurate for diffusion measurements.

3.6 Frequency response (FR)

Frequency Response is a pseudo-steady state relaxation method, in which one system variable (e.g., volume or pressure) is periodically perturbed around an equilibrium state, and the resulting periodic response in another system variable (e.g., pressure or flowrate) is measured to characterize the system. The perturbation is deliberately kept small to ensure that the model equations can be appropriately linearized. This general concept is illustrated in Fig. 9, where the response curve (amplitude ratio of the perturbed and responding variables) is plotted against the perturbation frequency. Introducing the perturbation frequency, as an additional degree of freedom, helps to decouple mass-transfer resistances into different regimes, distinguishable at various relative perturbation time scales. These regimes are represented schematically as lines of different shapes for various mass-transfer mechanisms. As a result, FR uniquely distinguishes among different mass-transfer mechanisms due to its high sensitivity to the forms of the governing transport equations. It enables the determination of system characteristics over much smaller changes in the system conditions, compared to other step response techniques. Moreover, it minimizes measurement errors as it is a periodic process without dependence on the

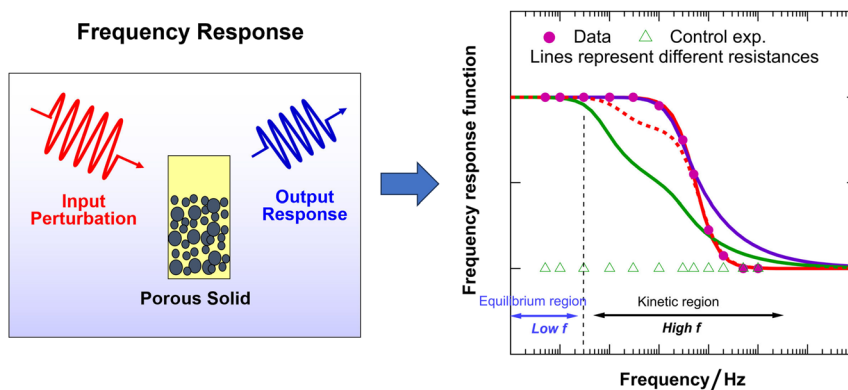


Fig. 9: General concept of Frequency Response, a pseudo-steady state relaxation method in which a small perturbation (usually <5 %) is applied to the system and the response of another system variable is monitored. The resulting response curve contains mass-transfer information which can be interpreted with the help of mathematical models, corresponding to different resistances. With an additional degree of freedom (perturbation frequency f), FR can discriminate among different mass-transfer mechanisms by examining the response over a large frequency spectrum. Equilibrium-related information, that is, local isotherm slope, can also be directly extracted from slow frequencies. As an alternative approach, the characteristic function can be further normalized by the equilibrium value, allowing data to start from 1 at low frequencies.

initial conditions. The technique has proven to be useful for characterizing transport of gases not only in adsorbent materials, primarily zeolites, but also in carbon, silica gel, and MOF.⁷⁶

Depending on which variables are perturbed in the experiment, FR can be divided into several types. The most widely used and simplest FR technique involves a closed system. In this method, the system volume containing the gas and adsorbent to be characterized is oscillated and the resulting response in system pressure is measured. This approach is often referred to as batch volume-swing frequency response (VSFR), and comprehensive reviews can be found in monographs.^{77–79} Other FR studies employ flow-through techniques, where perturbations are applied to inlet flow rates, pressure, or inlet concentrations in adsorbent/catalyst systems. For example, the pressure-swing frequency response (PSFR) technique perturbs the system pressure sinusoidally, measuring the outlet flow rate responses with the same frequency but with a different amplitude and phase lag.^{80,81} The most recent development is the concentration-swing frequency response (CSFR) method,^{82,83} incorporating a mass spectrometer to monitor outlet gas concentrations while sinusoidally varying flow rates of inlet gases, thus creating a concentration-perturbation. Compared to batch FR, the flow-through FR methods offer the advantage of minimizing heat effects and allowing flexible operation across a broad range of concentrations. The CSFR technique is particularly suited to studies involving gas mixtures, as the nature of the technique requires the use of multiple gases. By contrast, while mixture studies are possible using VSFR and PSFR, data analysis is complicated and hence more prone to error. The greatest advantage of VSFR over PSFR and CSFR is its ability to measure FR spectra at higher frequencies of near 10 Hz and above, whereas PSFR and CSFR have difficulty measuring spectra above 1 Hz. Data in the high-frequency region are required to identify fast mass-transfer coefficients that may not manifest at lower frequencies.

The ability of FR techniques to characterize kinetics relies on the availability of mathematical models to describe the FR of all transport mechanisms that could occur in the system under investigation. Based on the experimental setup, the corresponding material balance and energy balance can be written accordingly to give different overall transfer functions (G), relating the phase lag and amplitude ratio of the response and perturbation variables to the adsorbed-phase transfer models (G_n). G represents transfer function, and subscript n is variable related to adsorbed amount to give G_n as transfer function for adsorbed phase. By comparing the experimental data of FR curves with various mathematical models depicting each of the possible transport mechanisms, only the model corresponding to the correct mass-transfer mechanism will best describe the data as each model behaves differently over the entire range of frequencies. Throughout the history of the application of

FR techniques to adsorption systems, mathematical models have been derived to represent multiple dynamic processes, including diffusion, surface barrier, and heat effects, as well as a more complex combination of these mass-transfer resistances.^{84–86}

FR techniques require theoretical models to describe the influence of the kinetic processes on the amplitude attenuation and the phase lag, directly related to the equilibrium capacity and kinetics occurring within the system.⁷⁷ The solution of mass and energy conservation equations yields mathematical expressions of transfer functions to correlate the system response to the input signal. Due to the small magnitude of the input perturbation (<5 %), these equations can be treated using linear integral transform techniques, such as the Laplace transform to obtain analytical solutions. The evaluation may use frequency-domain solutions delineated by real (in-phase) and imaginary (out-of-phase) components as a function of angular frequency (ω) or Laplace domain solutions where a complex variable s is involved (i.e., $s = \omega i$). The transfer function G for the PSFR is expressed by the amplitude of the outlet mass flowrate response, ΔF , divided by the amplitude of the applied pressure perturbation, ΔP ,⁸⁰

$$G(s) = \frac{\Delta F}{\Delta P} = -s \left(M_s G_n + \frac{V_0}{R_g T} \right), \quad (43)$$

where M_s denotes the mass of adsorbent, R_g is the gas constant, T is the isotherm temperature, and V_0 is the volume of the system. It has been demonstrated that batch VSFR and flow-through PSFR can be united using a general approach based on master amplitude ratio curves. Consequently, the amplitude ratio (AR) curves from flow-through PSFR and batch VSFR coincide precisely when the AR is defined as $|\Delta F/\Delta P|/\omega$ for PSFR and $\left| \frac{\Delta V}{\Delta P} \right| \left(\frac{P_0}{R_g T} \right)$ for VSFR.⁸⁷ The adsorbed-phase transfer function G_n (in Eq. 43) describes how the adsorbable component in the gas phase adsorbs and diffuses through the adsorbents in response to changes in partial pressure. Under isothermal conditions, the G_n for diffusion in a spherical subject is given by⁸⁸

$$G_n(s) = \frac{\Delta n}{\Delta P} = \frac{3K}{\frac{s}{\eta}} \left\{ \sqrt{\frac{s}{\eta}} \coth \left(\sqrt{\frac{s}{\eta}} \right) - 1 \right\}, \quad (44)$$

where $\eta = D/R^2$ is the inverse of the diffusion time, n is the amount adsorbed, and K is proportional to the gradient of the adsorption isotherm. Depending on the FR technique employed and isotherm units, K could be expressed differently, such as dn/dP for PSFR, dn/dy for CSFR, or $M_s(R_g T/V_0)(dn/dP)$ for VSFR, respectively. It is noteworthy that the analytical solution for macropore (intercrystalline) diffusion-dominated systems shares the same form as Eq. 44 albeit with η replaced by an effective macropore diffusivity η_M defined differently. The real and imaginary parts of G_n are also referred as the in-phase and the out-of-phase characteristic functions, which have been extensively employed in the traditional analysis of VSFR.^{77–79} Further details on various mass-transfer models and related transfer functions can be found in the literature.^{76,87}

By combining Eqs. 43 and 44, the amplitude response for the isothermal diffusion cases can be predicted theoretically, offering insights into how different diffusion times (the inverse of D/R^2) influence the system's behavior. Fig. 10 illustrates the ideal shape and location of the amplitude ratio curves for isothermal diffusion (Fig. 10 a) and surface barrier (Fig. 10 b) with perturbation frequencies. The family curves have the same shape to the dominating resistance but differ in location with respect to the intrinsic mass-transfer rates. Slow rates are located in the low-frequency region, whereas fast rates are found in the high-frequency region.

A recent overview of FR applications in mass-transfer studies with microporous materials can be found in Ref. 88. In most cases, the identification of dominating mass-transfer resistances is unambiguous from the shape and pattern of the response curve, and the related mass-transfer rate can be accurately obtained. However, caution should be exercised to avoid unrecognized intrusion of macropore resistance for samples in pellets or even in assemblages of crystals. To distinguish between micropore- and macropore-dominating resistances, it is recommended to disperse samples in glass wools for separating individual crystals or to run additional experiments by varying crystal or pellet sizes since both types of resistances have the same shape of the response curves. Additionally, an experimental check by adding inert metal balls to adsorbents operated at identical conditions is recommended to recognize any intrusion of heat effects. This is effective to differentiate the effects of

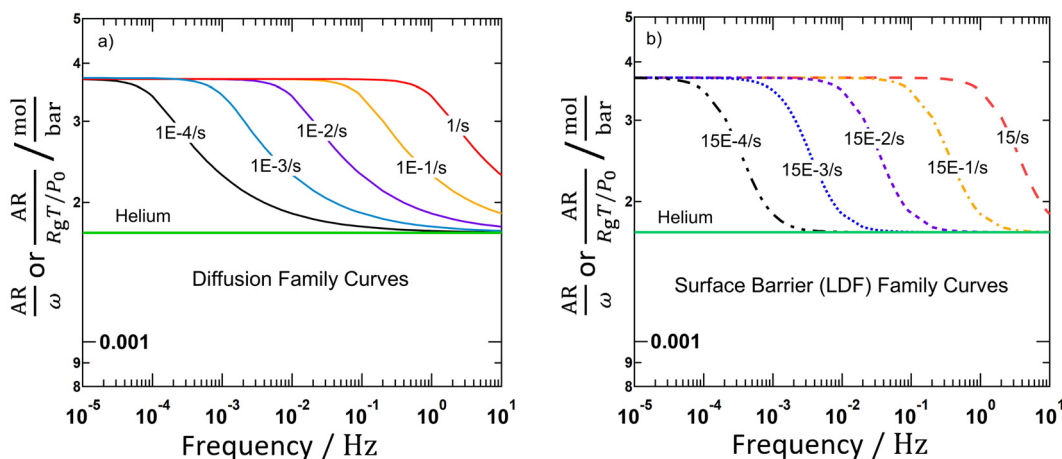


Fig. 10: Typical theoretical master amplitude ratio curves, $\left| \frac{\Delta V}{\Delta P} \right| \left(\frac{P_0}{R_g T} \right)$ for PSFR, and $\left| \frac{\Delta V}{\Delta P} \right| \left(\frac{P_0}{R_g T} \right)$ for VSFR, with parameters of $M_s = 2$ g, $K = 1$ mol/(kg bar), $P_0 = 1$ bar, and $V_0/R_g T = 0.00172$ mol/bar: (a) diffusion family curves with corresponding diffusion times ranging from 10^{-4} to 1 s $^{-1}$ and (b) surface barrier (LDF) family curves with k ranging from 15×10^{-4} to 15 s $^{-1}$. Solid green lines represent blank response from control experiment with helium, providing the value of $V_0/R_g T$. Adapted from Wang (Ref. 88) with permission.

mass transfer from any potential heat-related influences.⁸⁹ If the FR experiments with and without stainless steel balls behave the same, this suggests that the bimodal behavior is caused by an additional mass-transfer step because the inert beads have a minimal impact on the adsorbents' properties. However, if heat effects cannot be neglected, then experimental results would differ in the presence of metal beads due to alterations in heat dissipation. A nonlinear FR (NFR) approach using a relatively large amplitude modulation could provide a promising avenue for unambiguous model identification and estimation of the nonlinear model parameters, but practical application of the NFR approach comes with substantial technical challenges and mathematical complexity.⁹⁰

It needs to be noted that, for diffusion-dominated systems, FR, much like the other macroscopic methods (such as uptake in 3.3 and ZLC in 3.4), directly measure diffusion times (R^2/D) rather than the diffusivity D . To ensure accurate comparisons with other techniques, providing precise information of crystal or pellet size is considered the best practice. Depending on the dominant resistances, the relevant radii, that is, those of the pellets or the crystals, should be chosen correspondingly. The measurable diffusivities depend on both the crystal/pellet size and the frequency range covered by the specific FR apparatus. It is relatively easy to investigate slower diffusion processes, but it is challenging to extend the range of reliable measurement to faster processes that would require measurements at higher frequencies or synthesis of large crystals. By incorporating large crystal sizes and wider perturbation frequencies, FR techniques can be applied to study multi-kinetics processes covering mass-transfer rates spanning over ten orders of magnitude.⁷⁹

3.7 Membrane permeation

Two chambers separated by a membrane can be used to carry out measurements of the stationary or non-stationary flux through a nanoporous membrane layer or a single nanoporous crystal, which can be used to determine the transport diffusion coefficient D_T of the gas under study in the respective nanoporous zeolite, MOF or COF material.⁹¹

3.7.1 Sample preparation

Two principal strategies are followed: (i) Embedding of one or a few large single crystals into a non-permeable epoxy, glass, or metal matrix, and (ii) *in situ* growth of a continuous and dense nanoporous layer on a macroporous ceramic or metal supports. These two strategies are shown in Figs. 11 and 12.

The use of one or a few large single crystals embedded into a non-permeable epoxy or metal film can provide direction-dependent transport diffusion components D_T if the crystal structure is non-cubic. In a pioneering study, Hayhurst measured the diffusivity along the long axis of a large MFI crystal embedded in a polymer.⁹⁴ Later, Shah *et al.* used the time lag technique to determine the diffusivities of hydrocarbons in a large silicalite-1 crystal in epoxy.^{95,96} By embedding oriented large MFI crystals into a copper, silver, or nickel foil by combined sputtering and galvanic metal depositions, the anisotropy of diffusion in the MFI framework could be measured.^{92,97} Aligned $\text{AlPO}_4\text{-5}$ molecular sieve crystals, with the 1D-channel direction aligned perpendicular to the plane of the membrane, could be made gas tight in a nickel foil.⁹⁸

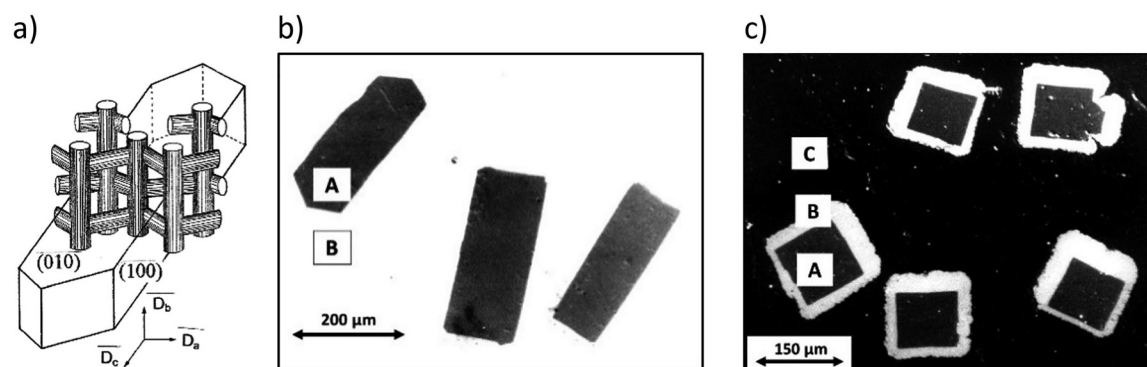


Fig. 11: Large MFI single crystals in different orientations for measuring anisotropic diffusion in a metal/epoxy film prepared by combined sputtering/galvanic/abrasion/polishing techniques. (a) Anisotropic pore system of the MFI structure, (b) two crystals in a and one crystal in b orientation, and (c) in vertical, that is, c orientation. (Ref. 92) A: MFI crystal; B: copper (galvanic deposition in (b) and sputtered in (c)); C: epoxy resin.

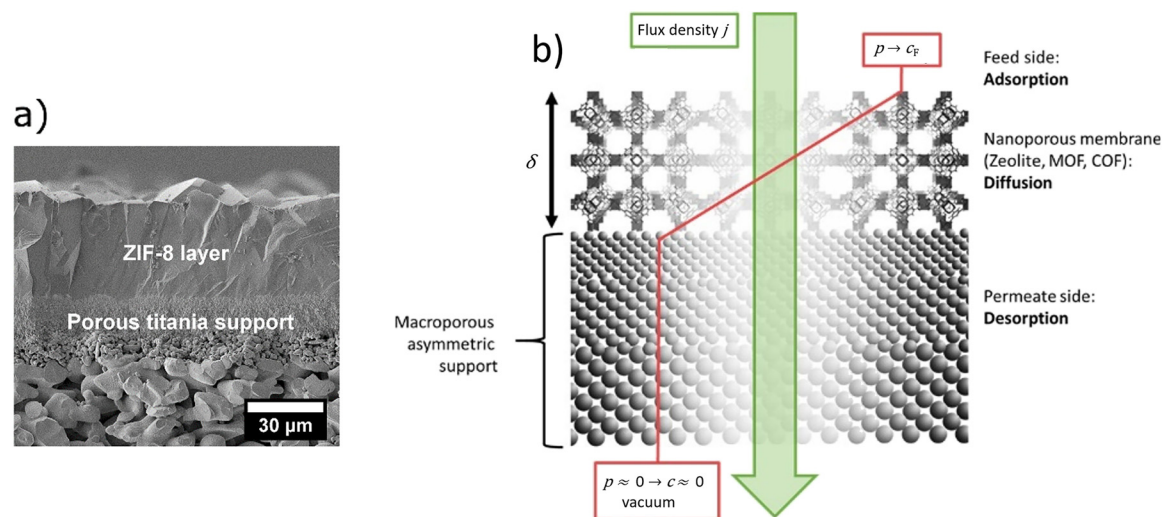


Fig. 12: Supported nanoporous membrane for diffusion studies. (a) Cross section of a 30- μm thick MOF membrane layer of structure type ZIF-8 grown solvothermally on an asymmetric titania ceramic support. (Ref. 93) The titania support is asymmetric (multi-layer) to reduce the flow resistance. (b) Gas transport through a supported nanoporous membrane in steady state.

Since the nanoporous layer of 1 μm –100 μm thickness is mechanically unstable (i.e., not self-supporting), the nanoporous membrane layer is usually synthesized on a macroporous asymmetric support (see Fig. 12). It is essential to ensure in permeation studies for the determination of diffusion coefficients that the flow resistance of the support can be neglected. Therefore, in diffusion studies thick ($>10\ \mu\text{m}$) membrane layers are advantageous. The trend in the membrane development for gas separation is opposite, only thin layers ($<1\ \mu\text{m}$) allow high flux densities. Case studies for the determination of diffusivities from supported membrane layers are discussed in Caro.⁹¹

3.7.2 Non-stationary transient permeation measurement

A non-stationary transient permeation measurement is carried out between two known volumes separated by a membrane. A step change in pressure in one of the chambers is followed by a transient response of the pressure in the system until equilibration. If the high-pressure side has a large volume, as a first-order approximation, the transient in the permeate side can be modeled assuming a constant pressure on the feed side. Measuring the pressure on the permeate side can then allow the calculation of the permeation flux j of the gas transported through samples as shown in Figs. 11 and 12. This is the most common technique to determine pure component transport diffusion coefficients according to Fick's 1st law by correlating molecular fluxes with the concentration gradients via $j = D_T \frac{dc}{dx}$ (Eq. 1 and Fig. 1a). However, for a quantitative estimation of the transport diffusivity D_T , simplified assumptions regarding the concentration gradient dc/dx have to be made. Assuming a linear concentration gradient over the membrane, dc/dx can be substituted by the concentration difference Δc across the nanoporous membrane layer divided by the thickness δ of the membrane layer. In a further approximation, it is assumed that the surface of the nanoporous membrane is in adsorption equilibrium with the gas phase of pressure p . After a quick pressure increase on the feed side of the membrane, the gas pressure p_F on the feed side must be constant to ensure a constant loading c_F as a fixed boundary condition which can be assured by a very large volume of the feed chamber. The permeate side chamber of the membrane is under strong vacuum, that is, the initial concentration of the diffusant in the nanoporous membrane is zero. These assumptions and simplifications give Eq. 45

$$j = -D_T \frac{dc}{dx} \approx -D_T \frac{\Delta c}{\delta} \approx -D_T \frac{c_F}{\delta} \quad (45)$$

with c_F denoting the guest concentration on the feed side. After the pressure jump on the feed side, gas molecules start to diffuse through the nanoporous membrane to the permeate side. After a certain time, needed to establish a linear concentration profile in the membrane, the pressure rise becomes linear. Linear regression of this region yields an intercept with the time axis (referred to as the time lag, t_{lag}), which can be shown (see, e.g.⁹¹, or Section 14.9.3 in⁶) to be related to the membrane thickness and the diffusivity by the relation.

$$t_{\text{lag}} = \frac{1}{6} \frac{\delta^2}{D_T}. \quad (46)$$

A short mathematical derivation of the time lag theory is given in⁹¹. An early application of the time lag method for the determination of diffusion coefficients from permeation studies of different gases through silicone rubber membranes was given by Barrer as accounted for by Ruthven.⁹⁹ However, this simple experiment for the determination of D_T data is a very rough estimate. With increasing permeation time, the pressure on the permeate side increases, the concentration difference becomes smaller, and a deviation from the linear pressure increase in the permeate chamber is observed due to the changed boundary conditions. In this case, the full solution to the transport problem available in Crank¹⁰⁰ (p. 51, Eq. 4.24) should be used.

An even more severe problem is the neglected concentration dependence of D_T . We describe the diffusive mass transport through the membrane by a single value of D_T , but this situation does not reflect the real state. The transport diffusivity D_T is strongly concentration dependent (notably due to the thermodynamic factor as appearing in Eq. 23), and there is always a concentration difference across the membrane. Therefore, the lowest diffusivity controls the mass transport, and for a type I (i.e., Langmuir-type⁴) isotherm this is the diffusivity in the

low-loading area of the nanoporous membrane facing the permeate side. See also Kärger *et al.*⁸ and Krishna *et al.*¹⁰¹

The problem can be solved when working with incremental pressure steps. As an example, the membrane is saturated on both sides with the gas under study of 100 mbar. Now, the pressure on the feed side is increased instantaneously to 110 mbar and will lead after some time lag to an almost linear pressure increase with time on the permeate side. From the pressure increase in the permeate chamber, the amount of gas passing through the membrane can be calculated. In this example, the resulting flux density through the membrane is controlled by a D_T at an averaged loading corresponding to the adsorption isotherm at 100–110 mbar. This method requires an accurate working pressure recording. Furthermore, this technique can also be extended to determine mixed gas diffusivities. The challenge in this case is the measurement of the gas composition on the permeate side. Usually, mass spectrometry is used since the extraction of tiny amounts of gas can be neglected. Also, IR spectroscopy is a powerful *in situ* gas analysis method.

3.7.3 Stationary steady-state permeation measurement

Transport diffusion coefficients D_T can be also derived from steady-state permeation measurements. As in the transient non-steady approach, the flux density across the membrane is measured by mass flow meters (calibrated by soap bubble counter), and in case of mixtures gas-chromatography or mass spectrometry are used to analyze the gas composition. In this case, the measured flux allows to determine, for a linear system, the product of D_T and the equilibrium constant, which in the membrane community is referred to as the solubility.

The use of a sweep gas will complicate the measurement as (i) adsorption of the sweep on the permeate side of the nanoporous membrane and (ii) a concentration gradient of the sweep gas over the nanoporous membrane causing a counter diffusion flux, suppress the flux of the gas component under study. Where possible no sweep gas should be used.

Often, the so-called Wicke–Kallenbach technique¹⁰² is applied for the study of multicomponent permeation in porous pellets. The characteristics of this technique is the use of a feed gas on the permeate side of the membrane at the same gas pressure as on the feed side, with the flux induced by differences in the relevant partial pressures. However, this technique has its limits if it is not properly applied. In the classical experiment of Wicke and Kallenbach, the feed gas was a mixture of CO_2/N_2 at 1 bar (partial pressures $p_{\text{CO}_2} = 0.13$ bar, $p_{\text{N}_2} = 0.87$ bar). On the permeate side of the carbon membrane was pure N_2 at 1 bar as sweep gas to transport the permeated CO_2 to the thermal conductivity detector. This experimental setup was justified since the only major gradient in partial pressure is that for CO_2 . There is also a slight gradient in the partial pressure of N_2 between the sweep side ($p_{\text{N}_2} = 1$ bar) and the feed side ($p_{\text{N}_2} = 0.87$ bar) which causes a counter flow of N_2 , but this slight N_2 counter flow does not disturb the surface diffusion-controlled CO_2 transport since CO_2 adsorbs much better on carbon surfaces than N_2 . These principles of the historic Wicke–Kallenbach technique are often violated nowadays. As an example, if one has a 50 %/50 % H_2/CH_4 mix at 1 bar on the feed side of a molecular sieve membrane with 0.4 nm pores, and N_2 as sweep gas on the other side of the membrane, H_2 will permeate faster through the membrane than CH_4 and an H_2/CH_4 selectivity greater than 1 can be determined. However, there will be also a flux of the sweep gas N_2 from the permeate to the feed side of the membrane. This counter flow situation reduces the H_2 and CH_4 fluxes. The effects of the counter flow of the sweep gas from the permeate to the feed side of the membrane can be suppressed to some extent when the feed gas is under an elevated pressure of up to 5 bar and the permeate side of 1 bar. The limitations of measuring single-gas diffusion coefficients with a Wicke–Kallenbach diffusion cell are addressed in Soukup *et al.*¹⁰³ However, on the other hand side the Wicke–Kallenbach cell is excellently suited to study counter-current diffusion.

3.8 Microimaging

The term microimaging has been introduced in connection with the development of experimental techniques allowing the “microscopic” investigation of diffusion phenomena under non-equilibrium conditions, that is, the

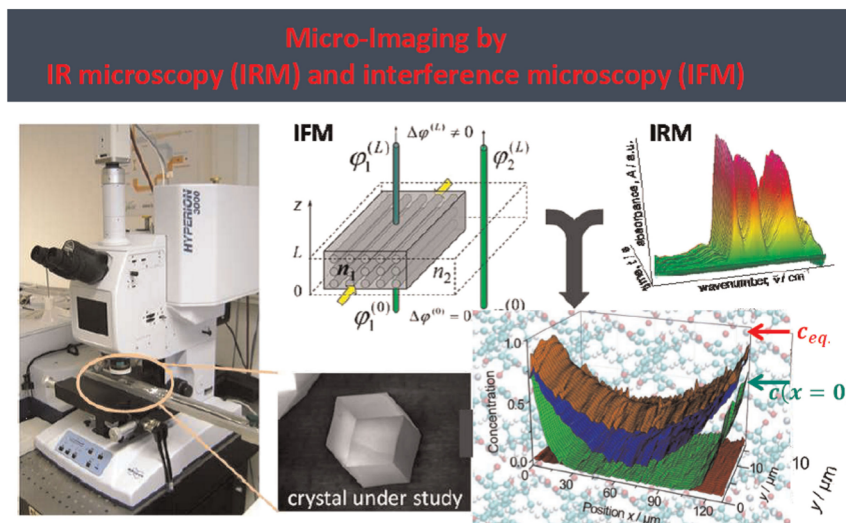


Fig. 13: Recording of transient concentration profiles via microimaging by interference microscopy (IFM) and IR microscopy (IRM), reprinted from Kärger (Ref. ¹⁰⁵) with permission.

recording of transient concentration profiles within the individual crystals or particles.¹⁰⁴ These options are provided by both interference and infrared microscopy, as schematically shown in Fig. 13. Interference microscopy (IFM) takes advantage of the fact that the wavelength of light passing the crystal varies with the guest concentration. Concentration profiles thus result from the interference patterns with a calibration beam (center of Fig. 13). Infrared microscopy (IRM) is based on the information provided by an array of detectors. The attained signal (top right in Fig. 13) provides information about the type and relative amount of molecules. The limits of spatial resolution are $0.5\ \mu\text{m}$ and $2.7\ \mu\text{m}$ by IFM and IRM, respectively. For the measurement of intracrystalline concentration profiles (bottom right of Fig. 13), crystal sizes should therefore be of the order of at least $10\ \mu\text{m}$ for IFM and $50\ \mu\text{m}$ for IRM.

In both IFM and IRM, the integral in observation direction rather than the concentration itself is recorded. This does not mean any restriction with particles/crystals of one- and two-dimensional pore structure under observation perpendicular to them, just as for also three-dimensional pore networks if, by sealing the top and bottom faces of the crystal/particle under study, diffusion fluxes in the observation direction are excluded.

As an example of such studies, Fig. 14 displays the evolution of the concentration profiles recorded via IRM during the uptake of cyclohexane by a plate of nanoporous glass,¹⁰⁷ with the top and bottom faces coated with a thin silica layer.¹⁰⁸ As well shown is the best fit of the solution of Fick's 2nd law, which has been attained with the concentration dependence of the transport diffusivity shown in Fig. 14(b). It thus turns out that, for the system under study, Fick's 2nd law has to be applied in its "complete" form, Eq. 7.

In Fig. 13 bottom right, the transient concentration profiles are seen to provide immediate evidence of the difference between the actual boundary concentration $c(x = 0)$ and the value c_{eq} in equilibrium with the surrounding atmosphere. Since, moreover, the diffusive flux entering or leaving the crystal follows directly from the ratio between the area between two subsequent concentration profiles and the time interval, microimaging is, via Eq. 9, ideally suited for the direct determination of the surface permeability.

The recording of transient concentration profiles as shown in Fig. 13, bottom right, allows plotting of the normalized boundary concentration $c(x = 0)/c_{\text{eq}}$ as a function of relative uptake m_t/m_∞ ("Heinke-Kärger plots"^{109,110}). Figure 15 shows such a plot as resulting from measurement, together with the results of analytical treatment.

It may be shown¹¹¹ that the value w of the ordinate intercept

$$w \approx \frac{\tau_{\text{dif}}}{\tau_{\text{dif}} + \tau_{\text{sur}}} = \frac{R^2 / (15D_T)}{R^2 / (15D_T) + R / (3\alpha)} \quad (47)$$

is approximately the ratio between the uptake time (τ_{dif}) that would result in the absence of the surface

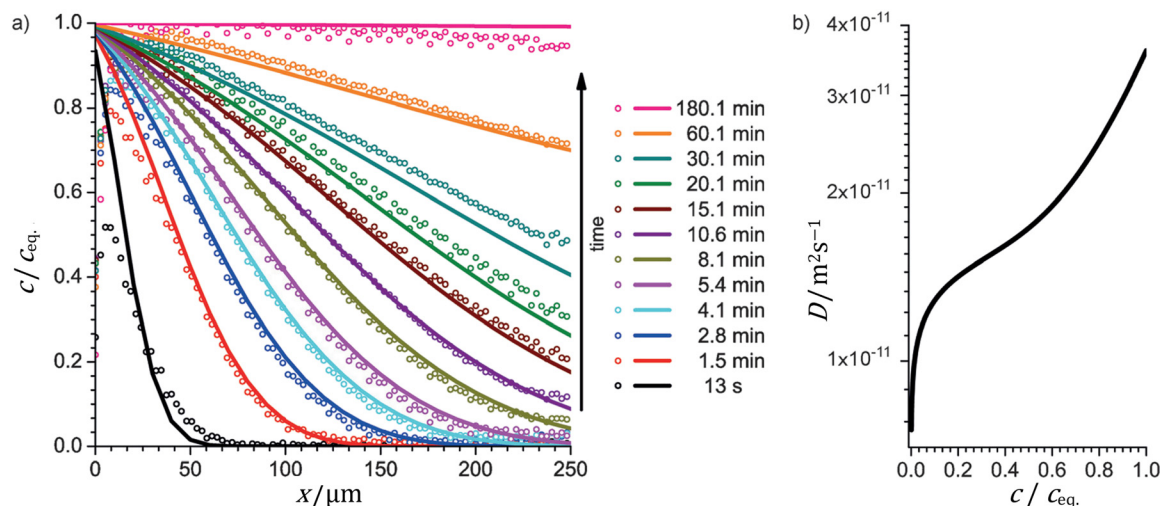


Fig. 14: Diffusion monitoring by IRM. (a) Evolution of the transient concentration of cyclohexane in a nanoporous glass during molecular uptake induced by a pressure step from 0 to 0.1 mbar in the surrounding atmosphere, recorded by IRM (circles) at 298 K and comparison with the predictions (solid lines) as resulting from the solution of Fick's 2nd law, Eq. 7, with the relevant initial and boundary conditions. (b) Concentration dependence of the transport diffusivity as implied for the prediction of the concentration profiles shown in (a). Adapted from (Ref. ¹⁰⁶) with permission.

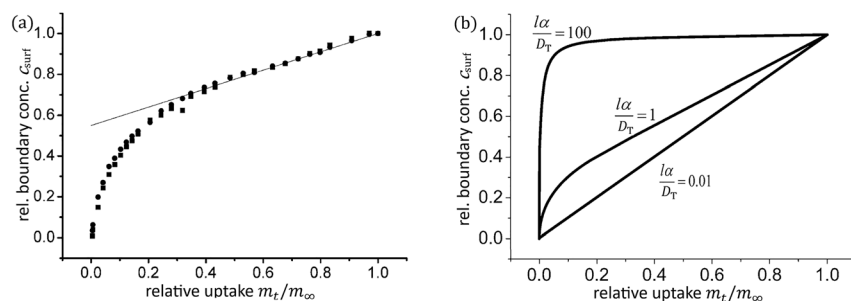


Fig. 15: "Heinke-Kärger plots" correlating actual boundary concentration (c_{surf}) and relative uptake (m_t/m_{∞}); (a) measured along the 8-ring channels of zeolite ferrierite with methanol as a guest molecule for a pressure step from 0 to 10 mbar at room temperature (two symbols for two crystal sides) and (b) calculated for a plate of thickness $2l$ considering mass transport, respectively, under dominating influence of intracrystalline diffusion ($l\alpha/D_T = 100$), of surface barriers ($l\alpha/D_T = 0.01$) and for comparable influences of intracrystalline diffusion and surface barriers ($l\alpha/D_T = 1$). Adapted from Heinke *et al.* ¹¹⁰ with permission.

resistances and the actual uptake time ($\tau_{dif+sur}$, determined by the influence of both intracrystalline diffusion *and* surface resistances), thus providing an immediate, useful estimate of the effect of the surface barrier on overall uptake and release.

Performing adsorption and desorption experiments on a single crystal makes microimaging particularly easily susceptible to interferences from disturbing influences. In view of the comprehensive information on mass transfer, directly provided by this technique, such disturbances are, as a rule, easily revealed already during the course of the experiments.

In comparison with most of the other techniques of diffusion measurement, IRM offers the great advantage of being able to perform self-diffusion (i.e., tracer exchange, see Fig. 1b) and transport diffusion (Fig. 1a) experiments within one and the same experimental device. Such experiments become easily possible due to the substantial differences in the IR frequencies of hydrocarbons with their deuterated counterparts.

A recent overview of the wide range of applications of microimaging to diffusion studies with nanoporous materials may be found in Chmelik *et al.*¹⁰⁹

3.9 X-ray Computed Tomography Imaging

X-ray Computed Tomography (CT) enables the recording of transient concentration profiles of adsorbed species within porous adsorbents, including individual adsorbent pellets and their packing. As such, the technique can be applied to the study of adsorption equilibria, kinetics, and dynamics by augmenting the dataset gathered from classic characterization methods, as depicted in Fig. 16, in addition to the options provided by, for example, NMR Imaging as presented in Section 3.10. Note that with current resolution, relatively large amounts of adsorbent are needed; thus so far, this technique has been only coupled to DCB experiments (Section 3.5). All the recommendations and discussions on how to properly design a DCB apply also here. In what follows the focus will be primarily on the additional requirements for X-ray CT.

The quantity measured in X-ray CT is the linear attenuation coefficient, which relates the intensity of the incident X-ray to the value remaining after it has passed through a dense object (Beer's law). Modern medical-grade X-ray CT scanners generate 2D cross-sectional maps of attenuation coefficients that represent a slice of the imaged object (tomogram). The three-dimensional image of the object is obtained upon stacking together many tomograms. As shown in Fig. 16c, these data are typically reported as CT numbers in Hounsfield units (HU) by using a simple linear transformation of the mass attenuation coefficient, such that distilled water and air take values of 0 HU and -1000 HU, respectively. For X-ray energies above 100 keV (readily attainable with a medical grade X-ray CT scanner), the linear attenuation coefficient is linearly proportional to the bulk density of

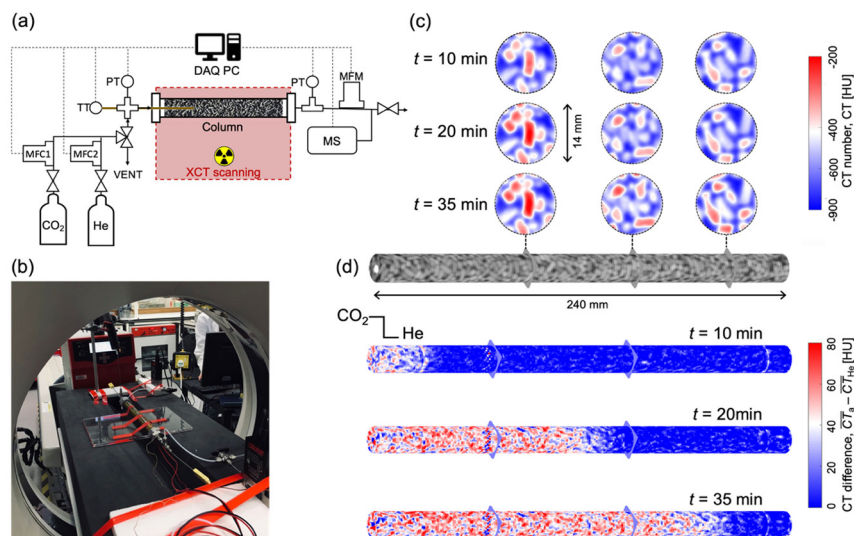


Fig. 16: Dynamic column breakthrough (DCB) experiments with the simultaneous imaging of internal adsorption concentration profiles by X-ray Computed Tomography (CT). (a) Schematic of the DCB apparatus consisting of an aluminum column packed with the adsorbent. Ancillary components include mass flow controllers (MFC1 and MFC2), mass flow meter (MFM), pressure transducers (PTs), thermocouple (TT), and mass spectrometer (MS). (b) Photograph of the assembled setup; for the imaging experiment, the column is fixed on the bed of the X-ray CT scanner, positioned within its gantry and subsequently aligned with the X-ray source and detector. (c) Raw 2D CT tomograms in Hounsfield units obtained during an adsorption experiment at three distinct times and positions alongside the 14 mm diameter, 240 mm long 3D reconstruction of the packed column (CO_2 displacing helium in a column packed with activated carbon rods: total pressure 100 kPa, temperature 293.15 K, and flow rate of $50 \text{ cm}^3/\text{min}$). (d) 3D reconstructions of the packed column during the same adsorption experiment described in (c) obtained upon subtracting a registered helium scan from the one obtained during the dynamic experiment.

the object.¹¹² This further implies that the CT number at any location within the object can be expressed as the linear combination of the attenuation from each of its components (adsorbent, bulk gas, and adsorbed phase).¹¹³ For the analysis of an adsorption experiment, difference images are computed upon subtracting a properly registered reference image acquired at saturation with an inert gas, such as helium (Fig. 16d).¹¹⁴ The obtained difference images are used to compute the amount adsorbed as a function of position and time by linear interpolation within the bounds of the calibration line acquired with reference fluids only.^{114,115} With a medical-grade CT scanner, a conventional DCB setup such as the one shown in Fig. 16 (20 to 30 cm long, 2 to 3 cm diameter column) can be scanned in a few seconds at a cross-sectional resolution of approx. 0.01 to 0.05 mm² and a longitudinal resolution of 0.5 to 1 mm. Note, that this is the scale of, commonly, the individual pellets and not of crystals as considered by microimaging. For quantitative analysis of local properties (e.g., adsorption isotherm), image downscaling by super-sampling should be applied to yield voxel elements with a volume of at least 10 mm³.¹¹⁵

As an example of such studies, Fig. 17 shows the internal one-dimensional adsorption profiles obtained via X-ray CT during a DCB experiment using the CO₂/He system on activated carbon in both adsorption (CO₂ displacing helium) and desorption modes (helium displacing CO₂). These internal profiles are compared to those generated by simulations using a generic one-dimensional column dynamics model.¹¹⁴ Mass transfer in the solid phase was formulated using a linear driving force (LDF) model, Eq. 42, neglecting film and micropore diffusion resistances. The internal profiles shown in Fig. 17 feature the characteristic sharpening phenomenon contrasting the adsorption and desorption runs. Although the experimental data from CT images are quite noisy, the simulations do broadly agree with the trend shown in the experimental dataset for both adsorption and desorption across the full range of flow rates. Overall, the model does an excellent job of predicting such detailed and complex adsorption dynamics behavior. The quantitative agreement with the model indicates that it should be possible to exploit DCB experiments augmented by *operando* X-ray CT imaging beyond the verification exercise presented here. The DCB experiments can in fact be used to reveal insights on the dynamics of adsorption processes, including the transport mechanisms of an adsorbate in the pores of an adsorbent.⁶⁵

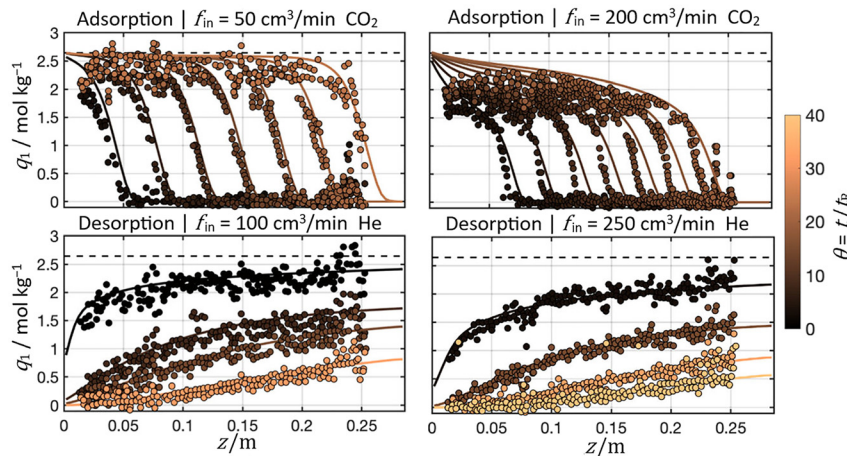


Fig. 17: Internal adsorption profiles from the DCB experiments carried out in Pini et al.¹¹⁴ The amount adsorbed at each location is plotted as a function of the distance from the column inlet. The top and bottom panels present adsorption and desorption runs, respectively. The flow rate, f_{in} , increases in the panels from left to right. The symbols correspond to the adsorption measurements computed from the X-ray CT images of the column. The solid lines correspond to simulations. The color of the symbols and solid lines indicate the reduced time, $\theta = t/t_R$, which is calculated by normalizing the time, t , with the mean residence time, t_R . The latter is evaluated as $t_R = \varepsilon AL/f_{in}$, where ε is the bed porosity, A is the column cross section, and L is the column length. The dashed horizontal line in each plot represents the expected equilibrium amount adsorbed at the nominal operating conditions of the column.

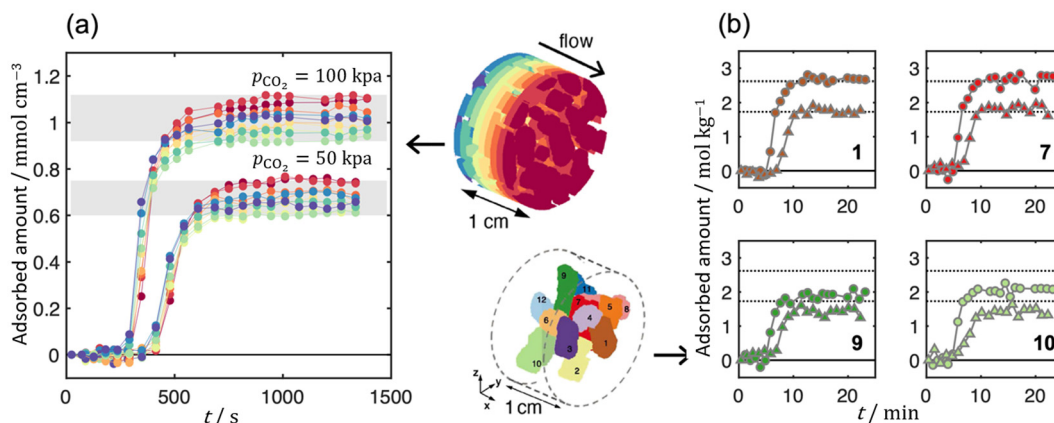


Fig. 18: Internal uptake adsorption curves measured by X-ray CT within a 1-cm thick section of the column presented in Fig. 16 (Ref. 114). (a) Curves are shown for ten 1-mm thick slices, and their color indicates location (see reconstructed image on the right) for pure ($p_{\text{CO}_2} = 100$ kPa) and mixed gas feed ($p_{\text{CO}_2} = 50$ kPa). Total pressure: $p = 100$ kPa, temperature: $T = 293.15$ K, and flow rate: $f_{\text{in}} = 100$ cm³/min. The gray-shaded area indicates the expected variation in the adsorbed amount because of changes in the local bed porosity. (b) Uptake adsorption curves measured for four individual adsorbent pellets within the same 1-cm thick section of the column. Circles and triangles refer to data obtained from the pure and mixed feed experiment. Curves are color-coded to represent each pellet (see reconstructed image on the left).

One of the benefits arising from the application of X-ray CT for measuring adsorption is the ability to make observations over multiple length scales to access adsorption properties spatially. Fig. 18 presents results obtained upon extracting from a DCB experiment transient CO₂ uptake profiles within a 1-cm thick section of the adsorption column, thereby extending the analysis to individual adsorbent pellets. Both slice- (Fig. 18a) and pellet-averaged uptake profiles (Fig. 18b) are characterized by a substantial degree of asymmetry with a slower transition to the equilibrium loading at late times. For a system characterized by fast intra-particle mass transport (such as the one considered here), this effect is attributed to the non-isothermal nature of the uptake process. We note that in Fig. 18a, the equilibrium amount adsorbed attained at late times differs among the ten individual slices. These variations are consistent with those observed in Fig. 17 across the whole column. Yet, the trend observed here is not random but is consistent by and large between two independent experiments carried out at different CO₂ partial pressure levels, as indicated by the color coding of the curves. Such variations along the length of the column can be explained by local changes in the bed density and, accordingly, local bed porosity (relative variation ± 10 %¹¹⁴). It can be seen in Fig. 18b that variations in adsorption uptake are apparent also at the level of individual pellets (pellets 1 and 7 vs. pellets 9 and 10, see again color coding in the reconstructed image). Because a unique average particle density was used to convert the X-ray CT measurement to an amount adsorbed per unit mass, this behavior is likely to ensue from variations in the intraparticle porosity. Most likely, both effects (inter- and intra-particle porosity) will contribute to local variations in the adsorption properties of the column.

3.10 Nuclear Magnetic Resonance (NMR) Imaging

In traditional Nuclear Magnetic Resonance (NMR) experiments, a homogeneous sample is placed in a homogeneous field of the magnetic flux density ($\vec{B}_0$) so that the precession frequencies (the resonance frequencies) of the nuclear spins of the same type are the same everywhere in the sample. However, since the precession frequency is linearly proportional to the applied magnetic field, if the magnetic field is changed in a linear fashion (i.e., if a constant magnetic gradient is applied) it is possible to relate position to frequency in the direction of the gradient (note that magnetic fields are vector quantities and have direction). This is akin to a piano keyboard. Should there be more spins in one location (e.g., a higher concentration) then there will be a larger signal at the resonance frequency (or position) correlating to that position. This is the basis of NMR Imaging (MRI, also known as *k*-space Imaging).

Nuclear Magnetic Resonance Imaging (MRI) is an exceptionally powerful technique for the investigation of mass transfer in the interior of nanoporous materials. It allows the recording of the distribution of guest molecules within the host material in both one (Section 3.10.1) and three (Section 3.10.2) directions with its variation in time as following, for example, in the experimental arrangements typically applied in also uptake and release measurements (Section 3.3) and/or on observing adsorption column dynamics (Section 3.5). Hence, on drawing from such observation conclusions about the intrinsic transport diffusion coefficients via Fick's first and second laws (Eqs. 1 and 7), attention must be paid to the possibility of interferences (heat of sorption, surface barriers, and bed effects) already mentioned in these sections.

In combination with NMR diffusion measurements (Section 3.11: Pulsed Field Gradient NMR), MRI can even reveal the spatial distribution of the self-diffusivities (Fig. 1b) within a porous medium. The method is non-invasive, relatively fast, and normally no sample labeling is required. Additionally, diffusion MRI can measure using a wide range of nuclei.

Like in all magnetic resonance-based techniques, sensitivity (i.e., signal-to-noise ratio, SNR) is often a limiting factor. Further, all imaging pulse sequences – the series of rf pulses, gradients, and delays executed by the MRI – are based on an echo pulse sequence and if the nuclear spin relaxation¹¹⁶ of a species is too rapid, imaging may not be possible (i.e., there is insufficient signal available to be acquired at the end of the echo). A conceptual introduction to MRI is given below together with some applications to nanoporous media. A more detailed exposition of MRI theory is given elsewhere.^{117,118} Lysova and Koptug¹¹⁹ and Gladden and Mitchell¹²⁰ reviewed the application of Nuclear Magnetic Resonance Imaging to chemical engineering and porous media.

3.10.1 1D Nuclear Magnetic Resonance Imaging

In the simplest case the imposition of a single magnetic gradient provides the means of 1D NMR Imaging, and since the signal amplitude is proportional to concentration, this technique can be used to measure the time-dependence of a concentration profile along a column and thus to gain access to the underlying diffusion phenomena (Fig. 19). The acquisition time for a single 1D projection (image) is of the order of 10 ms. If there were multiple components diffusing, it is in principle possible to individually select each component and provide its profile. In practice, however, there may be insufficient signal intensity or spectral differences to separate the components. X-ray CT measurements (see Section 3.9) are similar to MRI measurements of transport diffusion. Although the CT measurements are faster and capable of higher resolution and measurements over a shorter timescale, MRI offers the possibility of following multiple components at once, especially for 2D and 3D MRI (discussed further below).

The One-dimensional NMR Imaging has seen many applications in porous media. For example, it has been used to measure the time-dependent concentration profiles of butane in zeolites,¹²¹ and differences were observed depending on the size of the crystals. Further examples include the observation of water vapor and propane in zeolites,¹²² water in drying cardboard,¹²³ phosphate ions in dextran gels,¹²⁴ coke deposits in HZSM-5,¹²⁵ and the ingression of hyperpolarized xenon into Vycor®.¹²⁶ The ⁷Li *in situ* 1D NMR Imaging has been used to visualize the course of ion concentration and discharge in a battery cell. The cell was based on a PTFE body and a

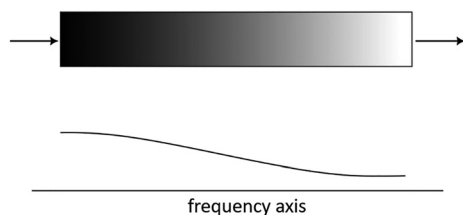


Fig. 19: A one-dimensional NMR image (bottom) of a concentration profile flowing through a column (top). In this instance, a magnetic gradient is directed along the long axis of the column. Consequently, the NMR “spectrum” is actually a 1D projection of the concentration gradient, and there is a linear correlation between the frequency axis and position along the column.

stack of glass microfiber discs that are soaked in an electrolyte and squeezed between an Li metal and a nano-Si-graphite composite electrode.¹²⁷

3.10.2 2D and 3D Nuclear Magnetic Resonance Imaging

Nuclear Magnetic Resonance Imaging can be extended to two and three dimensions by applying magnetic gradients along two or three different orthogonal directions (e.g., x , y , and z Cartesian coordinates), respectively, in a suitable pulse sequence.^{118,128} Such Nuclear Magnetic Resonance Imaging provides a means to notionally divide a sample into volume elements (or voxels) as shown in Fig. 20A. Thus, MRI is capable of studying the time-dependence of a concentration of species that is evolving in three dimensions. Ideally, the spatial resolutions of the voxels will exceed the sample spatial heterogeneity so that each voxel can be regarded as homogeneous. Generally, the limit of resolution is determined by SNR considerations, but when SNR is not limiting the ultimate limit of resolution will be determined by diffusion-based intravoxel motion on the imaging timescale.¹²⁹

Under ideal conditions, the signal from each voxel, $S(\vec{r})$, measures the density of the nuclei under study of a species, $\rho(\vec{r})$, at each position, $\vec{r}$. $\rho(\vec{r})$ would then be proportional to the net equilibrium nuclear spin magnetization in that voxel $M_0(\vec{r})$. Thus, $M_0(\vec{r})$ is in effect a concentration map. And, similar to the 1D profile, the evolution of $M_0(\vec{r})$ over a succession of images provides a means of measuring mutual (or concentration) diffusion.^{121,130} As for the 1D case, it is in principle possible to provide separate images for individual components.

The time required to obtain a 3D image is typically tens of ms and increases dramatically with voxel resolution. Voxel size is normally limited by the available SNR. The SNR is proportional to $B_0^{3/2}$.¹³¹ The voxel size for a clinical 3D image obtained in a 1.5 or 3 T static field is typically of the order of 1 mm^3 . There have been huge advances in sensitivity resulting from higher static magnetic fields (to larger than 20 T), more efficient pulse sequences, and probe sensitivity. Hyperpolarization techniques¹³² can also offer dramatic improvements but are of limited applicability.^{133–135} The greatest resolution is achieved when observing ^1H due to its natural abundance and higher sensitivity. In 2008, Weiger *et al.*¹³⁶ achieved isotropic resolution of $3\text{ }\mu\text{m}$ using dedicated hardware at 18.8 T. Nevertheless, the minimum voxel resolution in conventional NMR Imaging is still well in excess of that required to directly study nanopores. Further, it must be recalled that what is measured is an average over the respective voxels and this complicates the interpretation of MRI data from porous media.¹³⁷

Here, we review some applications of 2D and 3D MRI in porous media and discuss the challenges and opportunities. Nuclear Magnetic Resonance Imaging has been used to study the hydrogenation of α -methylstyrene on a single grain of Pt/ γ - Al_2O_3 catalyst,¹³⁸ and in combination with micro-computed X-ray

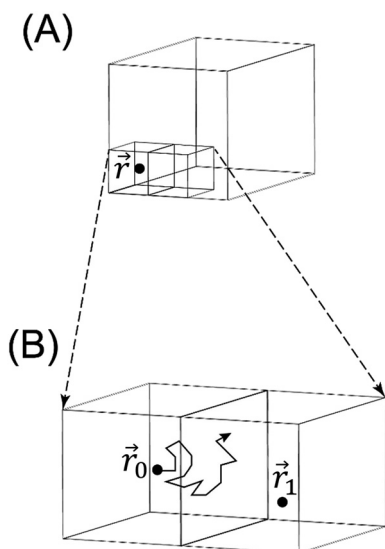


Fig. 20: Nuclear Magnetic Resonance Imaging (MRI) in three dimensions: (A) A 3D MRI sequence notionally divides the sample (i.e., the large cube) into voxels, and the intensity in each voxel is proportional to $\rho(\vec{r})$ for each voxel (cf. Fig. 19). Normally the lower limit of resolution will be determined by SNR, but for very small voxels the lower limit will be determined by intervoxel diffusion. In this diagram, a particle is depicted diffusing from point $\vec{r}_0$ to $\vec{r}_1$ during the pulse sequence. (B) By combining NMR diffusion measurements with MRI, it is possible to obtain the localized self-diffusion coefficient for each voxel, or in the case of anisotropic diffusion and with additional diffusion measurements the diffusion tensor describing each voxel. Adapted from Gupta *et al.*¹¹⁸ with permission.

Tomography, it has been used to study the entrapment of mercury within nanoporous silica materials following porosimetry.¹³⁹

Imaging can become challenging if there is insufficient time for a pulse sequence to be completed before the signal has decayed, preventing an accurate measurement. In addition to its inherently higher sensitivity and natural abundance, ^1H being a spin 1/2 nucleus generally has favorable relaxation properties. Quadrupolar nuclei (i.e., those nuclei having spin quantum number $>1/2$) are generally far less favorable due to their inherently faster relaxation. Nevertheless, specialized pulse sequences with ultrashort echo times can be used in these circumstances. Fabich et al.¹⁴⁰ demonstrated the use of ultra-short echo time imaging of *Nicotiana* seeds with effective spin-spin relaxation times, T_2^* , of only 185 μs in a fluidized bed reactor in 120 s, and by using a small tip angle and a compressed sensing reconstruction this was reduced to only 25 ms.

The versatility of MRI enabled by different pulse sequences provides a wide range of possibilities for extracting information about a sample. Yang et al.¹⁴¹ used metal-organic frameworks (MOFs) as tunable nanoporous hosts to provide cavities for xenon. The chemical shifts of hyperpolarized xenon were widely dispersed. Their results indicated that the pore size determined the exchange rate.

3.10.3 Localized self-diffusion measurement

By combining the Pulsed Field Gradient (PFG) NMR (also referred to as Pulsed Gradient Spin-Echo [PGSE] NMR, diffusion NMR, or q -space imaging)^{128,142–146} (see Section 3.11) with NMR Imaging, it is possible to measure localized (i.e., per voxel) self-diffusion¹⁴⁷ (see Fig. 20B). Were the localized diffusion measurements to be performed on a homogeneous sample, the measurement would return the same self-diffusion coefficient, D , for each voxel. However, in a real porous medium not only may the self-diffusion coefficient vary in different voxels but also the analysis is greatly complicated when geometrical boundaries affect the diffusive motion. Due to the complexity, it is often assumed that the diffusive process is still normal free diffusion. Consequently, the analysis results in an “effective” diffusivity D_{eff} (see also Eq. 58 and Fig. 21 in the subsequent Section 3.11), also referred to as ADC (“apparent diffusion coefficient”). In this case, the signal attenuation in each voxel will be of the following form:

$$E = \exp(-bD_{\text{eff}}), \quad (48)$$

where b is the total effect of the magnetic gradient with respect to diffusive motion. And it is understood that D_{eff} might vary by voxel. The computation of the attenuation may also have the effects of normalizing out spin relaxation on the voxel intensities.

The voxels in an MRI image acquired using a combined diffusion-MRI pulse sequence with a nonzero b value will be individually diffusion weighted according to Eq. 48. An “ADC map” (i.e., a map of the “apparent diffusion coefficients,” D_{eff}) can then be generated from the D_{eff} values from all the voxels. Voxels containing more rapidly diffusing species will appear darker as the signal will be more attenuated. However, restricted diffusion can complicate the interpretation since the D_{eff} will be less than D , resulting in less signal attenuation. Thus, regions of slower D , resulting in a higher D_{eff} in the presence of restricted diffusion, may appear darker in an ADC map and vice versa.

In the case of anisotropic diffusion, the situation becomes more complicated. To fully characterize such a system, it is necessary to determine the diffusion tensor for each voxel. A symmetric second-order diffusion tensor $\vec{\vec{D}}$ ^{150,151} is defined as follows:

$$\vec{\vec{D}} = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix}, \quad (49)$$

which contains all the information required to construct the diffusion ellipsoid. Typically, the orientation of the principal axes of the diffusion ellipsoid is unknown. If diffusion is measured in three orthogonal directions to produce a diffusion-weighted image reflecting the geometric mean of the signals from individual diffusion-

weighted images, the D_{eff} of the combined diffusion-weighted image will also be the mean of the D_{eff} values of the individual diffusion-weighted images,

$$E = \exp(-b(D_{\text{eff},x} + D_{\text{eff},y} + D_{\text{eff},z})) = \exp(-bD_{\text{eff,average}}), \quad (50)$$

where the subscripts x, y , and z indicate the directions of the applied diffusion gradients and the b value subsumes the effect of all three orthogonal diffusion gradients and any side effects from the imaging gradients.¹⁵² In this way, the combined diffusion-weighted images can be combined to give a $D_{\text{eff, average}}$ (also known as the mean diffusivity equal to $(D_{xx} + D_{yy} + D_{zz})/3$) map, which is a rotationally invariant measure. Another rotationally invariant characterization is the trace of the tensor $(D_{xx} + D_{yy} + D_{zz})$.

To fully determine $\vec{D}$, it is necessary to measure diffusion along at least six non-collinear and non-coplanar gradient directions, in addition to at least one non-diffusion-weighted image (i.e., $b = 0$). Such diffusion tensor imaging (DTI) is sometimes employed for mapping neural networks.^{153–155}

Uniform, nanoporous, hollow polycaprolactone fibers mimicking axon bundles in human white matter have been used as phantoms in diffusion tensor imaging and tractography studies.¹⁵⁶

3.11 Pulsed Field Gradient Nuclear Magnetic Resonance

Key to diffusion measurement by Pulsed Field Gradient (PFG) NMR is the recording of molecular displacements as illustrated by Fig. 1c. The principle of measurement may be understood already by following the classical model of nuclear magnetism. A more general introduction, including quantum mechanical considerations, may be found in the standard text books^{117,142,146,157,158} and in numerous reviews.^{120,142,144,159} NMR terms are defined in a recent IUPAC Recommendation.¹⁶⁰ Within the classical model, nuclei (nuclear “spins”) are understood to combine the properties of a magnetic dipole and a mechanic gyroscope. Under the influence of a magnetic field they perform, correspondingly, a rotational (“precessional”) motion about the direction of a magnetic field, like a rotating gyroscope about the direction of gravity. The angular frequency of this rotation (the “Larmor” frequency) is given by the following relation:

$$\omega = \gamma B_0 \quad (51)$$

B_0 stands for the magnetic flux density of the external field and γ , the gyromagnetic ratio, is a characteristic quantity of the considered nucleus. It is fixed for all NMR isotopes by an IUPAC convention.¹⁶¹ The original Larmor equation is, in opposite to Eq. (51), a vector equation with ω and B_0 as vectors and a negative sign on the right-hand side. But often this vector equation, which distinguishes between a clockwise and negative rotation for positive γ and counterclockwise and positive rotation for negative γ , is simplified, like in Eq. 51, to consider positive frequencies only.

With the individual spins, also their non-zero vector sum rotates around the direction of the magnetic field, ending up in a rotating net macroscopic magnetization. This rotating magnetization induces a voltage in a suitably positioned coil (the receiver coil of the NMR spectrometer), which is recorded as the NMR signal. It might be noted that typical energies of interaction of nuclear spins with the magnetic field, $\hbar\omega$, are orders of magnitude lower than the chemical bonds, rendering NMR to be a non-invasive and non-perturbative tool to study microdynamics.

In PFG NMR, over two short time intervals δ , the homogeneous field B_0 in z -direction is superimposed by an inhomogeneous field (the field gradient pulses), with

$$B_{\text{add}} = \vec{g} \cdot \vec{r} \quad (52)$$

denoting its component in the direction of the homogeneous field. By combining Eqs. 51 and 52, the Larmor frequencies during the gradient pulses are thus seen to become space dependent, following the relation

$$\omega(\vec{r}) = \gamma(B_0 + \vec{g} \cdot \vec{r}). \quad (53)$$

The PFG NMR experiment is started with an alignment of the net magnetization due to the application of a suitable sequence of radio frequency (RF) pulses, giving rise to a maximum in nuclear magnetization. Space dependence of the Larmor frequencies during application of the gradient pulses, however, gives rise to a spreading in the direction of nuclear magnetization at different locations and, finally, an extinction of the net macroscopic magnetization. As a special feature of the PFG NMR RF pulse sequences, precessional phases accumulated during the first and second field gradient pulses are opposite in sign. For nuclei, which have remained at the same position, the phases accumulated during the first- and second gradient pulses thus compensate each other. Any shift of diffusing species along the gradient direction, however, leads to a difference in the precessional phase in comparison with the mean magnetization. With Eq. 53, it is easily found to be.

$$\Delta\phi = \gamma g x \delta \quad (54)$$

where x denotes the displacement in the gradient direction in the time interval between the two gradient pulses and δ stands for their duration. On considering the vector sum of all individual magnetizations, spins contribute to overall magnetization with only the cosine of their phase shift. The diffusion-induced attenuation of the NMR signal $S(q, t)$ under the influence of pulsed field gradients may thus be noted as

$$S(q, t) / S(0, t) \equiv \psi(q, t) = \int_{-\infty}^{\infty} \cos(qx) \bar{P}(x, t) dx, \quad (55)$$

where $q = \gamma g \delta$ has been introduced as a measure of the intensity of the field gradient pulses and $\bar{P}(x, t)$ denotes the probability density that, during a time interval t , an arbitrarily selected molecule, which contributes to the NMR signal, has been shifted over a distance x in the gradient direction. This time interval, which appears as the “observation time” in PFG NMR experiments, is given by the separation of the two field gradient pulses. In the PFG NMR literature, for this time interval the term Δ is in common use. As a prerequisite of the strict validity of Eq. 55, the observation time t is implied to be much larger than the pulse duration ($\delta \ll t$).

The $\bar{P}(x, t)$ is referred to as the mean propagator.^{144,162,163} It easily results as the Fourier transform of the PFG NMR signal attenuation, that is, as the inversion of Eq. 55:

$$\bar{P}(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \psi(q, t) \cos(qx) dq. \quad (56)$$

In a homogeneous system, propagation properties are uniform all over the sample so that the mean propagator coincides with Eq. 5, the solution of Fick's law for an initial concentration distribution given by Dirac's delta function. By inserting Eq. 5 into Eq. 55, PFG NMR signal attenuation under the conditions of “normal” diffusion is thus found to be given by the following relation:

$$\psi(q, t) \equiv \frac{S(q, t)}{S(0, t)} = \exp(-q^2 D t) = \exp\left(-q^2 \frac{\langle x^2(t) \rangle}{2}\right), \quad (57)$$

where, with the last equality, we have made use of Einstein's diffusion equation, Eq. 6.

With Eq. 57, semilogarithmic plotting of the PFG NMR attenuation curve $\psi(q, t)$ versus the squared gradient pulse intensity is seen to yield a straight line, with its slope given by the self-diffusivity or the mean square displacement during the observation time, which is given by the distance between the two gradient pulses. The last equality does even hold as a reasonable approximation in complex systems with the mean propagator deviating from Eq. 5. In such cases, it is common use to introduce an effective self-diffusivity by the relation

$$D_{\text{eff}} = \frac{\langle x^2(t) \rangle}{2t} \quad (58)$$

coinciding with the genuine self-diffusivity in a homogenous system.

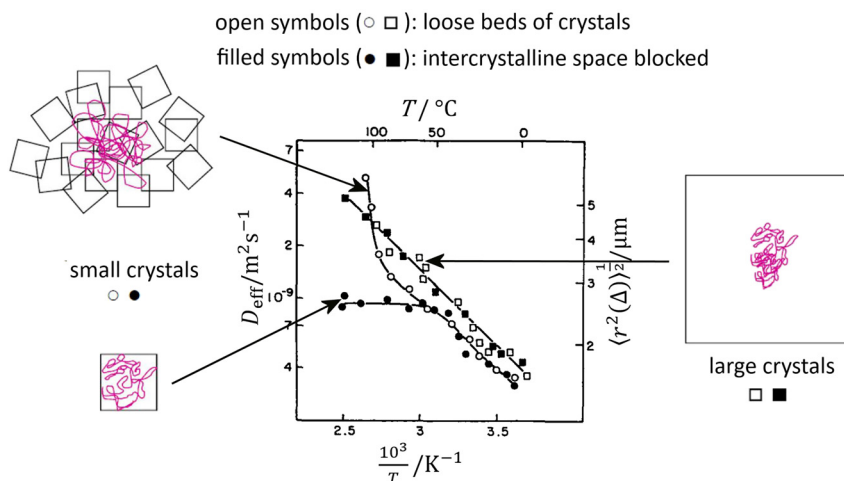


Fig. 21: Temperature dependence of the effective PFG NMR diffusivity (D_{eff}) and mean square displacements for water in zeolite MFI: small ($\circ$, $\bullet$ $7 \times 4 \times 3 \mu\text{m}^3$) and large ($\square$, $\blacksquare$ $16 \times 12 \times 8 \mu\text{m}^3$) crystals in a loose bed (open symbols) and with the intercrystalline space blocked (filled symbols) for an observation time $t = 1.2 \text{ ms}$, see Caro *et al.*¹⁴⁸ Adapted from (Ref. 149) with permission.

As a classic example of such studies, Fig. 21 displays the mean square displacement and the effective diffusivities of water in zeolite MFI for an observation time $t = 1.2 \text{ ms}$ as a function of temperature.¹⁴⁸ Measurements were performed with crystals of two sizes, introduced into the PFG NMR sample tubes as a loose bed in either their pristine form (empty symbols) or with coated crystal surfaces (filled symbols). Temperature dependence of the diffusivity in the large crystals (squares) is found to follow, over the whole range of temperatures covered, the usual Arrhenius dependence. The diffusion path lengths considered are, obviously, sufficiently small in comparison with the size of the crystals so that diffusion may indeed be assumed to take part in an infinitely extended, homogeneous system.

At sufficiently low temperatures, a similar behavior is also observed for the small crystals. The slight differences in the diffusivities of the two samples are most likely a consequence of minor differences in the loading. Now, however, with further increasing temperatures the molecular displacements approach the size of the crystals, giving rise to an upper limit of the mean square displacements and, accordingly, of the effective diffusivity for the sample with the blocked surface. In the pristine bed of crystals, however, the mean square displacement and, correspondingly, also the effective self-diffusivity are seen to even exceed the data obtained with the larger crystals. This is a consequence of the fact that, for diffusion path lengths exceeding the crystals, the effective diffusivity finally coincides with the “long-range” diffusivity

$$D_{\text{l.r.}} = p_{\text{inter}} D_{\text{inter}} \quad (59)$$

with p_{inter} and D_{inter} denoting, respectively, the relative amount of molecules in the intercrystalline space and their self-diffusivity.

Since PFG NMR is sensitive to the particular type of nuclei under study, it is ideally suited for the investigation of multicomponent diffusion by considering mixtures of molecules accommodating different nuclei.^{164–167} Thanks to high-resolution NMR, selective PFG NMR diffusion measurements are even possible with identical nuclei in different chemical surroundings^{168–172} enabling the recording of diffusivities during chemical reactions.¹⁷³

Variation of the direction of the magnetic field gradient with respect to sample and/or crystal direction offers manifold options of orientation-dependent diffusion measurement, including the measurement of diffusion tensors.

Since PFG NMR diffusion measurement is based on the analysis of a signal attenuation (Eq. 57), typical errors can be caused by poor choices of experimental parameters in the signal attenuation measurement. They may, for example, include a mismatch between the gradient pulses and a superposition of the tails of the gradient pulses with the signal. Independent checks for confirming that the observed signal attenuations are indeed caused by

diffusion are therefore urgently needed. For this purpose, ideally suited is a comparison of the information about structural details like the mean crystal size as resulting like in Fig. 21 from the PFG NMR data and the microscopically determined value. Equally helpful are measurements with a variation of, for example, the strength of the magnetic field or the nucleus under consideration (for molecules accommodating different NMR-active nuclei). A very simple check for ruling out such artifacts is performing measurements using a reference sample with well-known diffusion behavior and which produces similar signal attenuation with the same set of the control parameters of the pulse sequence used.

A special care in reporting the experimental findings must be devoted whenever the shapes of the diffusion attenuations deviate from the one given by Eq. 57. In this case, the source for multi-exponential behavior needs to be clarified and the way how diffusion coefficients are obtained from the analysis needs to be reported.

This refers, in particular, to the so-called NMR tracer desorption technique, in which the two constituents of the PFG NMR signal attenuation are associated with, respectively, molecules which, during the observation time, have left the crystals in which they have initially been accommodated, and which have not.^{174–176} This type of measurement provides, by varying the observation time, an easy access to the curve of tracer exchange and thus, by comparison of the resulting time constants with the theoretical estimates for diffusion and barrier-limited uptake (see Eqs. 11 and 14), direct information about the limiting mechanisms.

Like in the given case, it is quite generally important to correlate the molecular displacements with the structural properties of the materials under study obtained with the microscopy studies. Where it is possible, the measurements need to be performed for different observation times.

An important source of errors is, moreover, correlated with the fact that the intensity of the signal in PFG NMR is a function of nuclear magnetic relaxation of the species under consideration. These relaxation properties may, for one and the same molecule, dramatically vary between different regions of the sample. As a consequence, different regions of the sample may contribute quite differently to the signal. In the worst-case scenario (facilitated by the essentially unlimited options of signal accumulation), the measured signal has nothing to do anymore with those molecules and sample regions one is really interested in. Such errors, however, may be excluded by a purposeful variation of the pulse program time intervals, which control the influence of NMR relaxation on the PFG NMR signal. On reporting PFG NMR diffusivities, it is thus a good practice to report both the relevant nuclear magnetic relaxation times and the observation times.

Recent extensive accounts on the application of PFG NMR to diffusion studies in nanoporous materials may be found in Baniani *et al.*¹⁷² and Kärger *et al.*¹⁴⁹

3.12 Quasi-Elastic Neutron Scattering (QENS)

3.12.1 Fundamental relations and the principle of measurement

Any interaction between matter and a wave leads to diffraction or scattering phenomena. For mobile scatterers, exchange of energy between the incident wave and the scattering center becomes possible, leading to a Doppler shift in the frequency of the outgoing wave. This effect is intuitively understood to increase with increasing mobility and is most pronounced when the wavelength is in the range of the relevant spatial dimensions. If initiated by the random movement of diffusing molecules, frequency shifts are of varying intensity and occur in either direction, giving rise to a line broadening in the frequencies of the scattered wave in comparison with the incident one.

Scattering experiments with neutrons can only be properly described by adopting the framework of quantum mechanics. Here, a flux of neutrons (mass m , velocity v , and momentum p) is considered as a matter wave with the wave vector

$$\vec{k} = \frac{\vec{p}}{\hbar} = \frac{m\vec{v}}{\hbar} \quad (60)$$

and the angular frequency

$$\omega = \frac{E}{\hbar} = \frac{mv^2}{2\hbar}. \quad (61)$$

With $|\vec{k}| = k = \frac{2\pi}{\lambda}$, Eq. 60 is seen to comply with the well-known expression

$$\lambda = \frac{h}{mv} \quad (62)$$

for the de Broglie wave length. By combining Eqs. 61 and 62, wave length and frequency (and, hence, energy) are seen to be correlated by the relation

$$\lambda^2 \omega = \frac{\pi \hbar}{m}. \quad (63)$$

Therefore, λ and ω cannot be chosen independently from each other. With “cold” neutrons the wavelength is of the order of a few tenths of a nanometer, which is the required scale for investigating molecular motion at the elementary level.

The overall effect of scattering appears in the scattering cross section σ which is defined as the quotient between the total number of scattered particles per unit time and the total number of incident particles per unit time and area, via the relation

$$\sigma = 4\pi b^2 \quad (64)$$

may be understood as the area which, when introduced into the beam, would remove from the beam the same number of neutrons as are scattered in the experiment under consideration. Parameter b , referred to as the scattering length, is seen to the radius of this area if it is considered as a circle.

Within the frame of quantum mechanics, the fraction of scattered neutrons may be determined by considering the modulus $\psi_s^*(\vec{r}, t)\psi_s(\vec{r}, t)$ of the wave function $\psi_s(\vec{r}, t)$ of the scattered neutrons. It results as the superposition of the wave functions arising from the various individual scattering events within the sample. Since any scattering event may be accompanied by a variation in direction and energy of the scattered beam, instead of the total scattering cross section as considered in Eq. 64 the more relevant quantity to be considered is the so-called differential cross section $d^2\sigma/d\Omega dE$, with $(d^2\sigma/d\Omega dE) d\Omega dE$ denoting the fraction of neutrons scattered into a differential solid angle $d\Omega$ having energies in the interval $E \dots E + dE$. By carrying out the relevant calculations, one obtains (see, e.g., Egelstaff⁴⁷⁷)

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_s}{k_i} \frac{1}{N} \frac{1}{\hbar} \int e^{-i\omega t} \sum_{m,n} b_m^* b_n e^{i\vec{Q} \cdot [\vec{r}_m(t) - \vec{r}_n(0)]} dt, \quad (65)$$

where $\vec{Q}$ and ω denote, respectively, the difference in the wave vectors ($\vec{Q} = \vec{k}_s - \vec{k}_i$) and frequencies ($\omega = \omega_s - \omega_i$) between the incident and scattered beam. Since, in QENS (Quasi-Elastic Neutron Scattering), one is concerned with only small energy exchange between the neutrons and scattering nuclei, $k_s \approx k_i$, so that, for the magnitude of $\vec{Q}$, it holds $|\vec{Q}| = Q = \frac{4\pi}{\lambda_i} \sin(\theta/2) = 2k_i \sin(\theta/2)$, with θ denoting the scattering angle, that is, the angle between the incident and scattered beams. b_n may be understood as the (complex) amplitude of the wave function arising from scattering with the n -th nucleus. To elucidate the relationship between internal dynamics and scattering behavior, it is helpful to replace the double sum over all scattering centers by summing separately over identical and different scatterers:

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_s}{k_i} \frac{1}{N} \frac{1}{\hbar} \int e^{-i\omega t} \left\{ \sum_m b_m^* b_m e^{i\vec{Q} \cdot [\vec{r}_m(t) - \vec{r}_m(0)]} + \sum_{m \neq n} b_m^* b_n e^{i\vec{Q} \cdot [\vec{r}_m(t) - \vec{r}_n(0)]} \right\} dt. \quad (66)$$

Finally, by introducing the probability densities $G_{S,D}(\vec{r}, t)$ that, after time t , the same (S) or a different (D) nucleus will be at a position shifted by the vector $\vec{r}$, the summation in Eq. 66 may be replaced by multiplication with the respective probability densities and integration over all possible displacements $\vec{r}$, yielding.

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_s}{k_i} \frac{1}{N} \frac{1}{\hbar} \int e^{-i\omega t} N \left[\langle b^2 \rangle G_S(\vec{r}, t) + \langle b \rangle^2 G_D(\vec{r}, t) \right] e^{i\vec{Q} \cdot \vec{r}} d\vec{r} dt \quad (67)$$

with N denoting the total amount of scatterers. By adding the term $\langle b \rangle^2 G_s(\vec{r}, t)$ to the second term within the brackets and by subtracting it from the first one, Eq. 67 becomes

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_s}{k_i} \frac{1}{N} \frac{1}{h} \int \int e^{-i\omega t} N \left[(\langle b^2 \rangle - \langle b \rangle^2) G_s(\vec{r}, t) + \langle b \rangle^2 G(\vec{r}, t) \right] e^{i\vec{q} \cdot \vec{r}} d\vec{r} dt. \quad (68)$$

In this notation, the differential cross section $d^2\sigma/d\Omega dE$ is given as a linear combination of the fourfold Fourier transforms of the two key functions of propagation within a molecular ensemble, namely, the so-called Van Hove self-correlation function $G_s(\vec{r}, t)$ as introduced already with Eq. 67, denoting the probability density that an arbitrarily selected scattering nucleus is shifted over a distance $\vec{r}$ during time t and the Van Hove pair-correlation function $G(\vec{r}, t)$ denoting the probability density that at time t a scattering nucleus is at position $\vec{r}$ if it or another nucleus has been at the origin at time zero.

The respective prefactors $\langle b^2 \rangle - \langle b \rangle^2 \equiv (\langle b^2 \rangle - \langle b \rangle^2)$ and $\langle b \rangle^2$ determine the intensity with which each of these relationships appears in overall scattering. Following Eq. 64, one may thus distinguish between the incoherent scattering cross section $\sigma_{\text{inc}} = 4\pi(\langle b^2 \rangle - \langle b \rangle^2)$, which provides information about the propagation patterns of each individual molecule, and the coherent scattering cross section $\sigma_{\text{coh}} = 4\pi\langle b \rangle^2$, taking account of the propagation patterns of the whole ensemble. The scattering amplitude b_n as introduced with Eq. 65 is a function of the given nucleus and of the orientation of its spin in comparison with the spin of the neutrons, which is known to be either $+1/2$ or $-1/2$. Therefore, depending on the nucleus, their mean values may take on quite different values, as do the corresponding scattering cross sections.

With $\sigma_{\text{inc}} \approx 80$ b (barn) ($1 \text{ b} = 10^{-28} \text{ m}^2$), hydrogen nuclei offer the by far largest incoherent scattering cross sections while, with $\sigma_{\text{coh}} \approx 1.8$ b, the effect of coherent scattering is negligibly small. For nitrogen, with $\sigma_{\text{inc}} \approx 0.5$ b and $\sigma_{\text{coh}} \approx 11$ b, the situation is reversed. A survey of the scattering cross sections of some relevant nuclei may be found in Bee.¹⁷⁸

Equations 67 and 68 represent the fundamental relations correlating the experimentally directly accessible quantity, namely, the differential scattering cross section recorded as a function of the momentum and energy exchange during scattering, with the Van Hove correlation functions quantitating the movement of the scattering nuclei and, hence, of the associated molecules. For nuclei with dominating incoherent scattering cross sections, such as hydrogen, this information concerns the propagation patterns of the individual molecules as contained in the Van Hove self-correlation function $G_s(\vec{r}, t)$. For displacements notably exceeding the size of the individual molecules (i.e., of typically nanometers, see Section 3.12.2 and Fig. 22 for the range of measurement as accessible by QENS) $G_s(\vec{r}, t)$ becomes a Gaussian, resulting as a solution of Fick's 2nd law for the probability distribution, with the Dirac delta function as an initial condition (see Section 2.1 and Eq. 5). This is the information which, over the range of micrometers, is as well provided by PFG NMR, being – in this context – referred to as the propagator. Being sensitive to also much smaller displacements, incoherent QENS is seen to extend the range of measurement to also details of the individual steps of propagation, becoming complementary to the information of solid-state NMR (see Section 3.13) and being nicely corroborated by molecular dynamics simulation (see Section 4.1).

For dominating coherent scattering cross sections, scattering reveals the propagation behavior of the scattering nuclei as an ensemble. Therefore, by covering sufficiently large displacement, coherent QENS is able to attain the transport or collective diffusivity. Note that, differing from the situation under, for example, macroscopic uptake and release measurements (see Section 3.3), QENS operates under equilibrium conditions. This is possible since, as a microscopic technique, QENS is able to follow microscopic fluctuations which occur under also macroscopic equilibrium and since, owing to Onsager's regression theorem,¹⁸⁰ microscopic and macroscopic density fluctuations are controlled by the same transport parameters.

Quasi-Elastic Neutron Scattering (QENS) is thus seen to be able to determine, in principle, both self- and transport diffusivities, covering displacements from the elementary steps of diffusion up to diffusive displacements following a Gaussian distribution, with the mean square width increasing in proportion to the observation time (Eq. 5). This makes this technique unique compared to all other experimental techniques applied in diffusion studies. In order to receive such a wealth of information, however, very specific conditions must usually be met. They refer to both the nuclei under study and the scattering devices. The situation is, obviously, in particular

complicated by the fact that the functions of interest, namely, the Van Hove correlation functions, result from the primary data, the differential scattering cross section, after fourfold Fourier transformation, which may involve great uncertainties. An introduction to the measuring procedure and the challenges of measurement is provided by the subsequent section. For a detailed treatise, we refer to the in-depth technical literature.^{178,181–183}

3.12.2 Measurement method: options and limitations

Data analysis is, commonly, performed in terms of the coherent (incoherent) scattering functions, resulting from the Van Hove correlation functions as their fourfold Fourier transform.

$$S_{\text{inc,coh}}(\vec{Q}, \omega) = \iint e^{i\vec{Q} \cdot \vec{r} - i\omega t} G_{S,D}(\vec{r}, t) d\vec{r} dt, \quad (69)$$

so that, by inserting into Eq. 68 with the corresponding scattering cross sections, the differential cross section may be noted in the form

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_s}{k_i} \frac{1}{N} \frac{1}{h} \left(\sigma_{\text{coh}} S_{\text{coh}}(\vec{Q}, \omega) + \sigma_{\text{inc}} S_{\text{inc}}(\vec{Q}, \omega) \right) \quad (70)$$

with the coherent (incoherent) scattering functions $S_{\text{coh,inc}}(\vec{Q}, \omega)$ as the main objects of our interest.

For attaining the key information of QENS, namely, the energy exchange between the scattered neutron and the scattering center as a function of the scattering angle and, thus, of the momentum transfer, there exist three main options, referred to as Time-of-Flight (TOF) measurement, Backscattering (BS), and Neutron Spin-Echo (NSE). They are broadly used to study molecular motions. Descriptions of their principles of operation may be found in several published works.^{179,184–186} As an example, Fig. 22 provides an overview of the different ranges of energy and momentum transfer as accessible by these three techniques at the Institut Laue–Langevin (ILL) in Grenoble. These data are accompanied by the length and time scales of the measurement that, via Fourier transform, are correlated with the ranges of energy and momentum transfer covered in the experiments.

Instead of fourfold Fourier transformation, on converting the scattering functions $S_{\text{inc,coh}}(\vec{Q}, \omega)$ into the Van Hove correlation functions as the information of microdynamic relevance, it is usually more favorable to use, for the latter, suitable approaches. Thus, covering quite a large field of possible scenarios,^{187–189} the Van Hove self-correlation function may be assumed to be given by a Gaussian.

$$G_s(\vec{r}, t) = \frac{1}{[4\pi\gamma(t)]^{3/2}} \exp\left[-\frac{r^2}{4\gamma(t)}\right] \quad (71)$$

with $\gamma(t)$ being related to the mean square displacement of the scattering nuclei via

$$\langle r^2(t) \rangle = \int r^2 G_s(\vec{r}, t) d\vec{r} = 6\gamma(t). \quad (72)$$

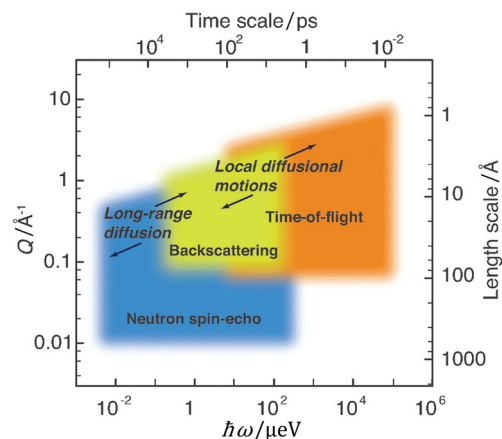


Fig. 22: Ranges of energy and momentum transfer covered by the neutron spectroscopy methods at the Institut Laue–Langevin (ILL) and the time and length scales thus accessible. Adapted from (Ref. 179) with permission.

By inserting Eq. 71 into Eq. 69, the incoherent scattering function is found to be completely determined by the mean square displacement via the relation

$$S_{\text{inc}}(\vec{Q}, \omega) = \frac{1}{2\pi} \int \exp[-Q^2 \gamma(t)] \exp(-i\omega t) dt. \quad (73)$$

For normal diffusion (following Fick's laws, see Section 2.1. and Eq. 6) it holds.

$$\gamma(t) \equiv \frac{\langle r^2(t) \rangle}{6} = Dt \quad (74)$$

and Eq. 73 becomes

$$S_{\text{inc}}^{\text{diff}} = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}. \quad (75)$$

If plotted as a function of the energy exchange $E = \hbar\omega$ during scattering, the incoherent scattering function is thus seen to become a Lorentzian with a half-width at half-maximum (HWHM)

$$\Delta\omega(Q) = DQ^2. \quad (76)$$

Plotted as a function of Q^2 , the HWHM becomes a straight line (see Fig. 23), with its slope representing the self-diffusivity.

Within the range of the elementary steps, the time dependence of the mean square displacement loses the simple form as provided by Eq. 74 and must be replaced by a more complicated expression corresponding to the chosen model. The results obtained with three different options of simulating molecular propagation by a sequence of jumps are as well shown in Fig. 23. These representations illustrate the twofold challenge of QENS on investigating molecular diffusion in nanoporous materials. Exploration of the details of the elementary steps and, with it, of the mechanisms of molecular diffusion necessitates the operation with momentum transfer of sufficient intensity, while just the opposite is true for ensuring measurement in the diffusion limit, that is, for the observation of sufficiently large displacements. Thus, both the maximum and minimum values of the momentum transfer as available by the given device turn out to be crucial for the performance of QENS in diffusion research.

Similarly, at sufficiently low Q values, the coherent scattering function is found to be ^{193,194}

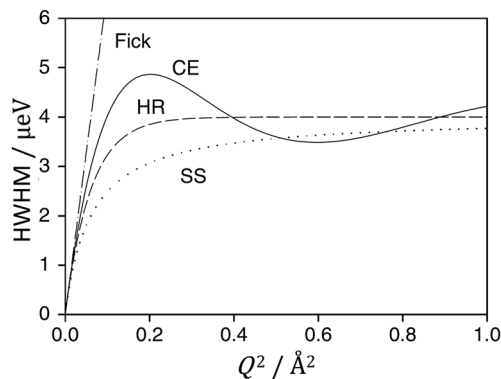


Fig. 23: Half-width at half-maximum of the incoherent scattering functions $S_{\text{inc}}(\vec{Q}, \omega)$ in the Gaussian approximation plotted as a function of the squared momentum transfer. Normal diffusion (following Fick's laws) is seen to yield a straight line. Depending on the chosen model (Chudley and Elliott (CE) (Ref. 190), Hall and Ross (HR) (Ref. 191) and Singwi and Sjölander (SS) (Ref. 192)), consideration of diffusion by molecular jumps leads to differing patterns, which (by choosing identical "long-range" diffusivities) are seen to approach the pattern for normal diffusion in the limiting case of small momentum transfer. Adapted from Jobic and Theodorou (Ref. 193) with permission.

$$\lim_{Q \rightarrow 0} S_{\text{coh}} \equiv S_{\text{coh}}^{\text{diff}} = \frac{S(Q)}{\pi} \frac{D_T Q^2}{\omega^2 + (D_T Q^2)^2}. \quad (77)$$

Differing from the expression for the incoherent scattering function, Eq. 75, the position of the self-diffusivity D is now occupied by the transport diffusivity D_T . As an additional factor, there appears the static structure factor $S(Q)$, which is the Fourier transform of the pair distribution function $G_{\text{D}(\text{S})}(\vec{r})$ and determines the structure of the sample (see Eq. 69). At $Q \rightarrow 0$, that is, at larger length scale, the static structure factor $S(Q)$ contains thermodynamic information, being related to the isothermal compressibility κ_T of the liquid by the compressibility equation:¹⁹⁵

$$S(0) = \kappa_T \rho k_B T = k_B T \left(\frac{\partial \rho}{\partial p} \right) \quad (78)$$

with ρ , k_B and p denoting density, Boltzmann constant and pressure, respectively. In the intermediate Q -range, the structure factor is a non-monotonic function of Q leading to a unique relation of the structure and collective dynamics. One of the most famous phenomena is the so-called de Gennes narrowing, in which the neutron inelastic scattering linewidth $\Delta\omega(Q)$ in liquids is found to narrow at the position of the peak in the structure factor. This effect is usually interpreted as the indication of enhanced cooperative dynamics or a confinement effect.^{196,197}

Due to limited resolution of the neutron spectrometers, the measured cross sections are affected by the instrumental resolution function, which can be determined by using the reference sample where all dynamical processes are frozen. Thus, selection of proper instrumental resolution and energy range in which dynamical effects are observed, and also wave length and corresponding momentum transfer range are crucial for a successful QENS experiment. It is worth to note that the broader energy transfer range is often related to a worse time/energy resolution. An overview of existing QENS facilities with their specification may be found in, for example, <https://neutronsources.org/>.

Covering molecular displacements up to couples of nanometers during observation times up to couples of picoseconds (see Fig. 22), the measurement range of QENS is comparable with the space and time scales as accessible by molecular dynamics simulations (see Section 4.1). The thus spanned measurement range for self-diffusion to a minimum of about $10^{-13} \text{ m}^2 \text{ s}^{-1}$ is within the range of PFG NMR (see Section 3.11), with the latter technique covering notably longer diffusion paths. Combination of these three techniques has thus been found to be capable of providing valuable insights into the details of intracrystalline diffusion, as exemplified in Fig. 24

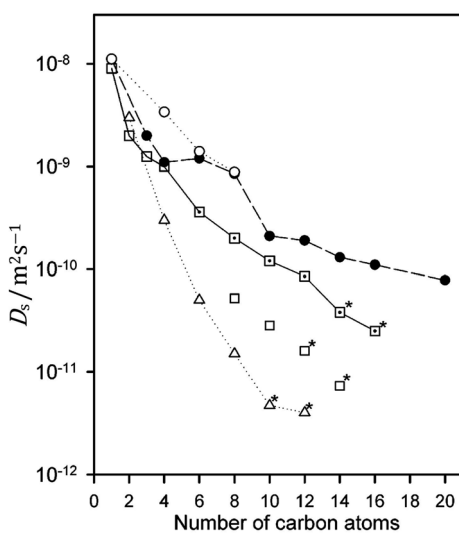


Fig. 24: Self-diffusion coefficients of alkanes in silicalite-1 at 300 K obtained by different techniques: (O) MD simulations (•) hierarchical simulations, (□) QENS, (△) PFG NMR, and (□) QENS in Na-ZSM-5. Asterisked symbols correspond to extrapolation to 300 K. Adapted from Jobic and Theodorou (Ref. 198) with permission.

with the self-diffusivities of alkanes of varying chain lengths in MFI-type zeolites as obtained with different techniques. In accordance with the IUPAC naming system, unless otherwise stated, in this Technical Report alkanes are understood to be linear (i.e., “normal”) alkanes, even without the initial n -.

For the diffusivities of the short-chain-length alkanes, the simulation results are seen to be in a fair agreement with the data experimentally determined with both QENS and PFG NMR, mutually confirming their validity. With increasing chain length, this agreement is found to be preserved on comparing the simulation and QENS data, while PFG NMR gives rise to distinctly smaller diffusivities, thus revealing the existence of transport resistances (internal barriers) with mutual spacings notably exceeding the diffusion path lengths covered by QENS, but within the range covered by PFG NMR. The possibility of the existence of such internal barriers has been confirmed by PFG NMR studies of intracrystalline diffusion with varying observation times^{199,200} and by structural analysis via micro-spectroscopy^{201,202} (see also Section 3.14) and electron microscopy.²⁰³

As mentioned above, analysis of the coherent scattering function results in the transport (collective) diffusivity. As an example, Gautam *et al.*²⁰⁴ study the diffusion of propane in presence of CO₂ in nanoporous silica aerogels. In the case of pure CO₂ in the aerogel, the main scattering contribution is coherent due to carbon and oxygen both being purely coherent scatterers. The data are treated in the framework of Singwi and Sjölander (SS) model mentioned above. Transport diffusion of CO₂ is found to be much faster than self-diffusion of the propane molecules. Moreover, the effect of CO₂ on the propane dynamics is to enhance the jump rate of propane molecules, thereby increasing its diffusivity.

Jobic *et al.*²⁰⁵ report on the measurement of the transport diffusivities of N₂ and CO₂ in silicalite at various loadings and temperatures and their comparison with the outcome of molecular dynamics simulations (MDs). The results obtained by measurement and simulation are found to be in a good agreement. The transport diffusivities show the usual pronounced increase with increasing loading for both guest molecules. The loading dependence is significantly mitigated when considering the corrected diffusivities (as obtained via Eq. 23 from the transport diffusivities and the adsorption isotherm), with the corrected diffusivities still tending to increase with increasing loading for N₂ and to decrease for CO₂.

3.13 Solid-state Nuclear Magnetic Resonance

Solid-state Nuclear Magnetic Resonance (NMR) spectroscopy, like QENS in the previous Section 3.12, provides information about the diffusion process from two sides. First, the comprehensive quantification of the diffusion behavior of guest molecules in nanoporous host materials can be established from information about elementary steps of diffusion, that is, about the mechanisms giving rise to molecular movement. Second, also statements about the rate of molecular propagation, that is, about the diffusion coefficients as introduced with Fig. 1, can be obtained. This is achieved by means of the Einstein equation (Eqs. 6 and 80) by connecting jump times with jump lengths, the latter being estimated on the basis of the given host–guest structure. Nuclear Magnetic Resonance methods are distinguished by a particularly large variety in the information. Both in the application of NMR to imaging (Section 3.10) and in the NMR pulsed field gradient technique of diffusion measurement (Section 3.11), key information has been deduced by observing the response of the system to a well-defined variation of externally applied inhomogeneities in the magnetic field. The common basis of these techniques and NMR techniques without pulsed gradients is the correlation between Larmor frequency ν_L and the absolute value of the magnetic flux density B . It holds for Larmor frequencies expressed in Hertz

$$\nu_L = \frac{\gamma}{2\pi} B. \quad (79)$$

See also Eq. (51). The parameter γ , the gyromagnetic ratio, is fixed for all NMR isotopes by an IUPAC convention.¹⁶¹ These values correspond to a “zero” chemical shift for all reference materials like tetramethylsilane (TMS) for ¹H, ²H, ¹³C, and ²⁹Si.

This section shows that, via NMR, information about the elementary steps of diffusion may be deduced by evaluation of the first-order quadrupole broadening of the ²H NMR spectrum as demonstrated in several studies

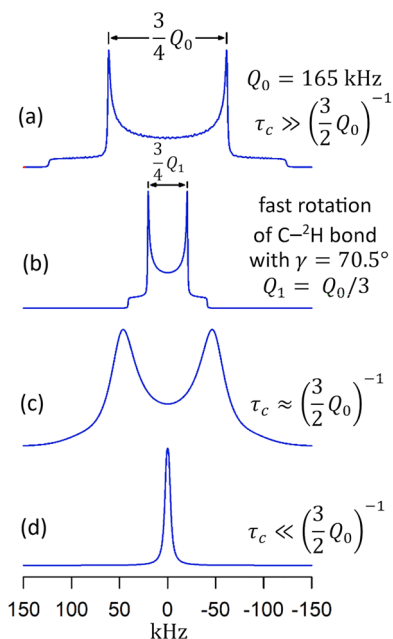


Fig. 25: The effect of molecular motion on the line shape of the ^2H NMR spectrum of CD_3 group in some organic molecule. (a) Immobile or static CD_3 group; (b) fast rotation of CD_3 group around C-C bond with the angle 70.5° ; (c) isotropic rotation of the molecule with $\tau_c \approx \left(\frac{3}{2}Q_0\right)^{-1}$, and (d) fast isotropic rotation with $\tau_c \ll \left(\frac{3}{2}Q_0\right)^{-1}$.

by Stepanov and his colleagues (reviewed in Kolokolov *et al.*²⁰⁶) and by evaluation of the exchange NMR spectra of ^1H , ^6Li , ^{13}C , ^{19}F , and ^{129}Xe nuclei as demonstrated in several studies by Chmelka and his colleagues (reviewed in Selter *et al.*²⁰⁷).

The solid-state ^2H NMR spectrum of immobile molecules has the form of a so-called Pake powder doublet, with separation between two singularities equal to $\frac{3}{4}Q_0$, where Q_0 is the quadrupole coupling constant for deuterium nucleus (Fig. 25a).²⁰⁸ Simple downscaling of the Pake doublet by the factor $\frac{3\cos^2\gamma-1}{2}$ can be achieved by fast rotation around an axis with the angle γ with respect to the C- ^2H bond (Fig. 25b). For rotating methyl or phenyl groups with angles of 70.5° and 60° , respectively,²⁰⁸ narrowing factors of 0.33 and 0.125 with respect to the “rigid” case may be achieved.

Via NMR, molecular mobility can be characterized by an analysis of the correlation time τ_c of molecular reorientation. We define the NMR correlation time τ_c as the mean time for a reorientation of the C- ^2H bond in the laboratory system by a solid angle of 1 (steradian). The spectral width of a “rigid” ^2H NMR spectrum is equal to $\frac{3}{2}Q_0$. We have slow mobility if $\tau_c \gg \left(\frac{3}{2}Q_0\right)^{-1}$, medium (intermediate) mobility if $\tau_c \approx \left(\frac{3}{2}Q_0\right)^{-1}$, and fast mobility if $\tau_c \ll \left(\frac{3}{2}Q_0\right)^{-1}$. In the case of isotropic reorientational motion (rotation) of the molecule as a whole, for correlation times τ_c comparable to $\left(\frac{3}{2}Q_0\right)^{-1}$, a broadening of the spectrum is observed and the sharp features of the Pake pattern disappear²⁰⁹ (Fig. 25c). For rapid isotropic reorientation, as in liquids, when $\tau_c \ll \left(\frac{3}{2}Q_0\right)^{-1}$, the powder pattern is averaged to zero and a single line of Lorentzian shape is observed at the Larmor frequency of the deuterium nucleus (Fig. 25d). The parameter τ_c can be derived from line shape analysis for slow and anisotropically reorienting molecules with correlation times of the order of 10^{-4} to 10^{-6} s. For fast, both anisotropically and isotropically reorienting molecules with $\tau_c < 10^{-7}$ s, analysis of longitudinal and transverse nuclear magnetic relaxation times is used for estimating the correlation time τ_c . To derive information on the diffusivity, the obtained τ_c values have to be associated with well-defined parameters of the translation motion, notably with the life time τ_D of a molecule within a particular cage in the host framework.

For some of the molecules confined in the pores, for example, butane in ZSM-5,²¹⁰ their motions can be characterized by several internal rotations and the translational motion. To derive the information on the diffusional motion of these molecules, the model including the expected motions should be built up and further analysis of the line shape or/and relaxation times is performed within the frame of the developed model. When

trapped inside a porous matrix, some certain angular displacements of molecules are realized by the jumps between the adsorption sites, that is, by the diffusional steps. An estimation of diffusion coefficients D can be performed using the Einstein equation,¹⁵ which is written for self-diffusion in three dimensions as.

$$D = \frac{\langle l^2 \rangle}{6\tau}. \quad (80)$$

The mean square displacement $\langle l^2 \rangle$ of the molecule in the material pores and the observation time τ may include varying numbers of diffusion steps, implying that subsequent displacements are independent. With this understanding, Eq. 80 may be as well used with the observation time τ given by the mean residence time τ_D of a molecule on one adsorption site and the mean displacement by the mean jump length l between adjacent adsorption sites. The value τ_D can be estimated from NMR data. The jump length l is determined by the known geometry of the nanoporous host material.

Whereas ^2H NMR relies on line shape analyses that are sensitive to relatively fast molecular motions on time scales in the range of 10^{-4} to 10^{-6} s, exchange NMR techniques probe slower reorientational jump dynamics of adsorbed molecules that occur on millisecond to second timescales.^{211,212} Such discrete molecular hopping events between adsorption sites in nanoporous solids, such as zeolites or metal-organic frameworks, result in changes in NMR frequencies of nuclei on molecules that occupy sites with different local bonding or magnetic field environments. For example, ^{129}Xe atoms adsorbed in zeolite nanopores^{213,214} with different sizes (Fig. 26a) can manifest different local environments that result in different isotropic chemical shifts with different NMR frequencies ω_1 and ω_2 . If exchange between the two inequivalent nanopore environments is slow relative to the reciprocal frequency difference $|\omega_1 - \omega_2|$ of the signals, then exchange NMR techniques can be used to analyze the molecular-level details of the adsorbate hopping process(es). A series of such discrete hopping events that result in net translational displacements of the atoms or molecules over longer length and time scales account for the bulk diffusion properties of the molecules within the nanopores.

A typical two-dimensional (2D) exchange NMR experiment has three distinct time periods, as depicted schematically in Fig. 26b: (i) the incremented evolution time t_1 (of order 10^{-4} s) during which nuclear spin polarization associated with molecules in their initial adsorption environments is indirectly monitored, (ii) a longer mixing time t_{mix} in the range of 10^{-3} to 1 s during which molecules can undergo dynamic reorientation to another adsorption site, and (iii) a detection time t_2 (of order 10^{-4} s) during which the nuclear spin polarization associated with molecules in their final adsorption environments is directly measured.^{211,212} Double Fourier transformation converts the time-domain signals (t_1, t_2) into frequencies (ω_1, ω_2) that are generally presented in the form of a 2D contour plot in Fig. 26c. For a given set of conditions (e.g., temperature and pressure), the mixing time t_{mix} is parameterized at the discretion of the experimentalist. For a sufficiently short value of $t_{\text{mix}} \ll \tau_c$ relative to the motional correlation time τ_c of the hopping process, negligible numbers of atoms or

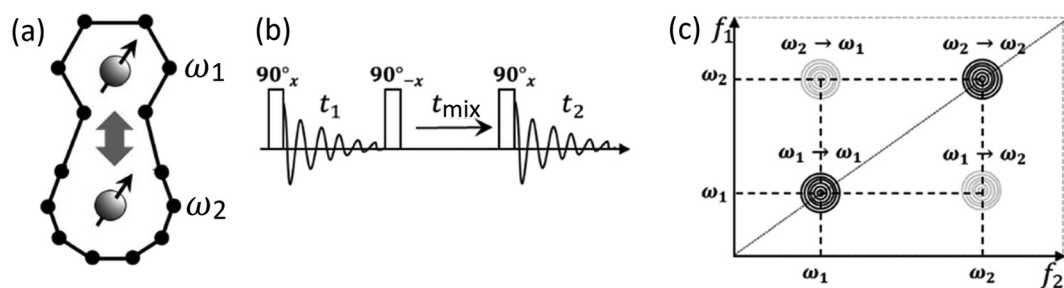


Fig. 26: Guest hopping recorded by 2D exchange NMR: Schematic diagrams of (a) two nuclear spins on atoms or molecules in different local nanopore environments that exchange their positions and lead to distinct NMR frequencies that manifest different chemical shifts or quadrupolar interactions, (b) a 2D exchange NMR experiment, showing the three 90° radiofrequency pulses and their phases and the evolution (t_1), mixing (t_{mix}), and detection (t_2) time periods, and (c) a contour-plot representation of a hypothetical 2D exchange NMR spectrum obtained after Fourier-transformation of the time-domain signals (t_1, t_2) into the frequency domain (ω_1, ω_2). Adapted from Selter et al.²⁰⁷ with permission.

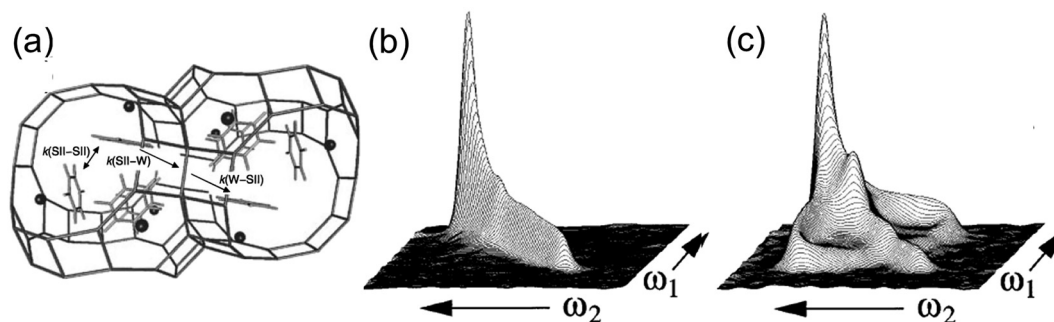


Fig. 27: 2D Exchange NMR study with benzene in zeolite Ca^{2+} -LSX: (a) Molecules of benzene adsorbed at Ca^{2+} SII cation sites in zeolite Ca^{2+} -LSX. Several rate coefficients for benzene exchange between intra-supercage SII sites $k(\text{SII-SII})$, from an SII site to a supercage window site $k(\text{SII-W})$, and from a window site to an SII site in a neighboring supercage $k(\text{W-SII})$. (b, c) Static 2D exchange ^{13}C NMR spectra acquired for single-site ^{13}C -enriched benzene adsorbed on Ca^{2+} -LSX zeolite at 298 K with a mixing time of (b) 1 ms, during which negligible site-hopping occurs or (c) mixing time of 300 ms, during which a substantial fraction of the benzene molecules has hopped to different sites. Adapted from Schaefer *et al.*²¹⁵ with permission.

molecules undergo dynamic exchange, such that those nuclei initially in environments with NMR frequencies ω_1 and ω_2 during the evolution period t_1 stay where they are and retain their respective frequencies during the subsequent detection period t_2 . This results in a diagonal 2D exchange NMR spectrum, as shown schematically in Fig. 26c (dark circles). By comparison, for longer values of $t_{\text{mix}} \approx \tau_c$, there is a higher probability that some atoms or molecules will undergo dynamic exchange between the two environments, so that those nuclei initially in environments with NMR frequencies ω_1 and ω_2 during the evolution period t_1 will have changed their frequencies to be ω_2 and ω_1 , respectively, during the subsequent detection period t_2 . This situation also results in off-diagonal signal intensity, as indicated by the gray circles in Fig. 26c. By comparing the integrated signal intensities along versus off the spectrum diagonal, it is possible to quantify the number of equivalent adsorption sites involved in a hopping process, the geometric angles through which the molecules hop between sites, the mean correlation time of the site-hopping process, all model-free, as well as their respective distributions.^{214–216}

The 2D exchange NMR can therefore provide an enormous amount of molecular-level information on the discrete dynamical hopping events that underlie slow diffusive processes. Whereas the above example concerns exchange NMR using ^{129}Xe atoms as the probe species, similar exchange NMR investigations with the nuclei ^1H , ^6Li , ^{13}C , and ^{19}F have successfully exploited the sensitivity of their NMR signals to obtain information on the nanoscale temporal events, from which larger-scale diffusion processes result.²⁰⁷ A technologically important example is the diffusion of hydrocarbon molecules in nanoporous zeolites, such as zeolites with the faujasite (FAU) structure that is used industrially in fluidized catalytic cracking or isomerization of hydrocarbon feedstocks and in air separation. It was investigated by two-dimensional ^{13}C exchange NMR spectroscopy. In particular, the site-hopping dynamics of benzene molecules adsorbed at cation sites in Ca^{2+} -LSX, Ca^{2+} -Y, and Ag^+ -Y zeolite powders have been analyzed in detail.^{215–217}

In static isotropic powders, individual zeolite crystallites and their nanopores have random orientations with respect to the large static magnetic field used in analyses of anisotropic NMR signals, which results in well-defined elliptical features, from which the geometry of the site-hopping process is straightforwardly determined: For the case of benzene molecules adsorbed at Ca^{2+} SII cation sites in Ca^{2+} -LSX or Ca^{2+} -Y zeolite (Fig. 27a), discrete molecular hopping events between adsorption sites represent the elementary processes, from which macroscopic diffusion ultimately results. The benzene molecules rotate rapidly about their 6-fold axes, yielding an axially symmetric ^{13}C line shape, which is also manifested in the 2D ^{13}C exchange NMR spectrum (Fig. 27b) acquired at 298 K with a short mixing time of 1 ms. By comparison, for a longer mixing time of 300 ms under the same conditions, a well-defined elliptical distribution of ^{13}C intensity is observed (Fig. 27c), from which the geometry of the site-hopping process is straightforwardly determined to be 109.5° . This reorientation angle corresponds to discrete hopping of adsorbed benzene molecules between tetrahedrally arranged Ca^{2+} SII cation sites, the

positions of which are consistent with X-ray crystallography.^{215,216} Such 2D exchange NMR measurements on macroscopically static powders are highly informative but time-consuming and suffer from broad signals that result in relatively low signal sensitivity. These limitations can nevertheless be overcome by using the 1D exchange-induced-sidebands (EISs) method under magic-angle spinning (MAS) conditions, which yields significantly improved NMR signal sensitivity, though at the expense of some geometric information.²¹⁸ Overall, the detailed insights from exchange NMR on slow discrete dynamic motions undergone by molecules or ions in nanoporous solids provide a strong molecular-level foundation for analyzing processes that occur over longer length or time scales, which are manifested by their macroscopic diffusion properties. Exchange NMR can be generally applied to analogous transport processes that occur in a wide range of materials for manifold purposes, including catalysis, batteries, and separations.

3.14 Single-molecule tracking

The fundamental relations of diffusion, as introduced in Section 2 and underpinned in Section 4 by molecular modeling, emerge as a superposition of the diffusion paths of large molecular ensembles. Correspondingly, molecular ensembles were also in the focus of all so far considered techniques of diffusion measurement.

In “real” systems, however, very often structural details of the host material under study, such as internal and external transport barriers or adsorption sites and molecular “traps,” are of substantial influence on the overall transport behavior of molecules. While such features become clearly visible on following the diffusion paths of the individual molecules by single-molecule observation, they may easily remain undetected on observing molecular ensembles. Single-molecule observation becomes even more important on studying the details of catalytic conversion, since it is only in this way that the sites of conversion become detectable by immediate observation.

Hence, in addition to the wide variety of powerful analytical methods, such as spectroscopy and microscopy, so far mainly applied for the exploration of the working principles of catalysis in porous solid materials including diffusion, adsorption-desorption, and surface catalysis,^{219,220} there emerged the need for the development and application of techniques for exploring the spatiotemporal dynamics of these fundamental processes,²²¹ that is, of micro-spectroscopy methods to investigate catalyst materials down to the level of single molecules and single atoms,^{222,223} especially to capture the fundamentals of diffusion processes in porous solids.²²⁴

As one of the most powerful techniques among these emerging micro-spectroscopy methods, we refer to single-molecule fluorescence (SMF) microscopy, which has been increasingly used in the past decade to elucidate the chemistry of porous materials, including zeolites, clays, mesoporous crystalline materials as well as metal-organic frameworks. It can be used as an analytical tool to explore in detail the pore space by monitoring the trajectories of individual fluorescent molecules. This ensemble-free micro-spectroscopy approach directly reveals spatiotemporal heterogeneities in the molecular diffusion as well as in the reactivity of individual molecules, which would have been obscured in bulk spectroscopy measurements, thereby showing the uniqueness of the SMF microscopy approach to assess spatiotemporal heterogeneities within functional solid catalysts. This will be illustrated for zeolite-based catalysts, in particular for industrially relevant Fluid Catalytic Cracking (FCC) particles, which are currently not only used for the catalytic conversion of crude oil fractions but also explored for catalytic pyrolysis of plastic waste. Time and space scales thus becoming directly accessible are in the range of, respectively, 10 to 30 ms and 2 to 30 nm, although the exact value depends on the material properties of the functional solid catalysts.

One of the first examples of such SMF microscopy studies include the diffusion work of single-molecules, such as the highly fluorescent terrylenediimide (TDI) derivative, in mesoporous crystalline materials, as performed by the groups of Bräuchle and Bein^{225–227}. Different molecular trajectories could be observed, thereby showing some analogy between individual cars in street maps and single-molecules in straight, curved, and even blocked pore channels. An illustrative example, showing the combination of single-molecule catalysis and molecular diffusion, originates from the work of Huang *et al.*²²⁸ This research group made use of the deacetylation reaction of Amplex Red as dye molecule, which is non-fluorescent, into resorufin, which is fluorescent, with H_2O_2 as the

oxidant. The catalyst system under study were Pt nanoparticles supported on a SiO₂ core, surrounded by a shell of mesoporous SiO₂. There exist several review papers on this topic^{229–233} with the most recent review articles published by Huang and co-workers in *Chemical Society Reviews*²³⁴ as well as the one published in *Adsorption*²³⁵ as part of this IUPAC initiative.

As a consequence of their technological relevance, in the past few years particularly intensive studies were devoted to MFI-type zeolites and their “derivatives,” including large coffin-shaped zeolite ZSM-5 crystals,^{236–238} thin-films of zeolite ZSM-5 with well-oriented straight and sinusoidal micropores,²³⁹ and the industrially relevant FCC particles,^{240–242} as the probably most complex systems so far investigated with the SMF microscopy methodology. To illustrate the methodology of the SMF microscopy tool, we will take this most complex FCC particle and show how insights in single-molecule diffusion within this porous material can be studied and demonstrate the spatiotemporal heterogeneities in this showcase. We refer the interested reader to the original paper to get familiar with the details of this SMF microscopy study.²⁴¹

Figure 28 shows the principle of the SMF microscopy study, in which the movements of individual fluorescent molecules within the catalyst particle at about 30 nm spatial resolution were followed. Note that this SMF methodology probes self-diffusion rather than transport diffusion (see Section 2.1). Since both processes are governed by the same underlying mechanism (i.e., random movement of molecules), the thus attainable information refers to either of these processes. For sufficiently low concentrations, which are mandatory in SMF microscopy for ensuring that the recorded trajectories may indeed be attributed to one and the same molecule,¹⁹ self- and transport diffusion are anyway known to coincide (see Section 2.1). The industrially used FCC material under investigation contains zeolite ZSM-5 as the active solid acid phase. An intact single fresh FCC particle of approximately 20 μm in diameter (Fig. 28A) was selected to match the field of view (25 × 25 μm²) of the fluorescence microscope setup. The pore network of this catalyst material was studied using *N,N*-bis (2,6-dimethylphenyl)-perylene-3,4,9,10-tetracarboxylic diimide (in short PDI, Fig. 28D) as highly fluorescent probe molecule. The poly-aromatic nature and molecular dimensions (ø 1–2 nm) of PDI are similar to components of vacuum gas oil (VGO), although PDI contains more (polar) functional groups. The FCC particles were submerged in

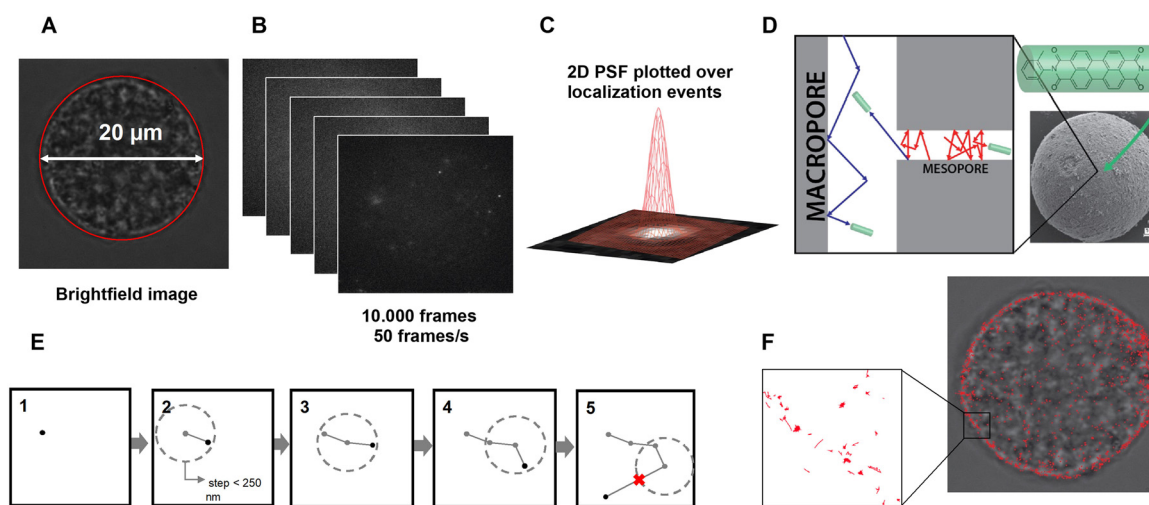


Fig. 28: Experimental approach to perform single-molecule fluorescence microscopy (SMF) of a single catalyst particle, more specifically a 20 μm-sized Fluid Catalytic Cracking (FCC) particle to convert, for example, vacuum gas oil into gasoline and chemicals, such as propylene. Single-Molecule Fluorescence (SMF) was used to follow the mobility of a dye in the pore space of the FCC particle. (A) Brightfield image of the FCC particle; (B) many frames taken to monitor the mobility of the fluorescent molecule; (C) 2D localization procedure for pinpointing the dye molecule in the material using the point spreading function (PSF) approach; (D) pictorial representation of the transport of the dye molecule, a perylene-type molecule (PDI), in the macro- and mesopore space of the FCC particle; (E) different 2D frames showing the way a single molecule is tracked as function of time, thereby following a procedure to ensure the transport is originating from the same molecule; and (F) different SMF trajectories within the FCC particle, leading to about 4100 individual tracks. A 532 nm laser excitation source was used for the SMF microscopy measurements of the FCC particle.

a solution of extremely low concentration of PDI. This dilution allowed following the movement of individual PDI molecules with an inverted wide-field fluorescence microscope, which was focused at the middle of the FCC particle to image a complete cross section. Selected movies were recorded with a frame rate of about 50 frames per second (Fig. 28B) over a total period of 2 h, thereby allowing for a sufficient number of images to be collected so that a high number of tracks of single PDI molecules could be tracked.

Movies of fluorescent single-molecules allowed their movement through the pore network of the FCC particle to be reconstructed (Fig. 28F), while Fig. 28E shows the analytical approach to obtain the trajectory of an individual PDI molecule, which can be localized in the 2D-frames with the point spreading function (PSF) approach. The observed molecular tracks could be classified into three different states by a machine learning technique and all were found to be distributed homogeneously over the single FCC particle, as shown in Fig. 29. Most of the PDI molecules (88 %) turned out to be immobile, with the molecule most likely being physisorbed or trapped or being only moving very locally, which can be coined as “extensive local motion”;²⁴³ the remainder set of PDI molecules was either mobile (i.e., 8 %), with the PDI molecules moving inside the macro- or mesopores, or showed hybrid behavior (4 %). Mobile tracks of the PDI had an average diffusion coefficient of $D \approx 8 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. The pronounced scatter of the data from $10^{-16} \text{ m}^2 \text{ s}^{-1}$ to $10^{-12} \text{ m}^2 \text{ s}^{-1}$ is thought to be related to the wide range of pore sizes found within the FCC particles.

Analysis of the trajectories of single molecules within porous hosts, such as zeolites, may be notably facilitated by the use of a recently developed software program with graphical user interface and documentation (DiffusionLab software package²⁴⁴), which is freely available. By using this DiffusionLab software package, one can perform an automated classification-based motion analysis of single-molecule trajectories in complex porous solids. Extensive use of this software package in combination with the increasing technical capabilities of the SMF microscopy methodology is expected to lead to a notably increased understanding of diffusion–reaction relationships of nanoporous solids, with the ultimate goal of developing functional materials with improved separation, adsorption, and catalytic performances.

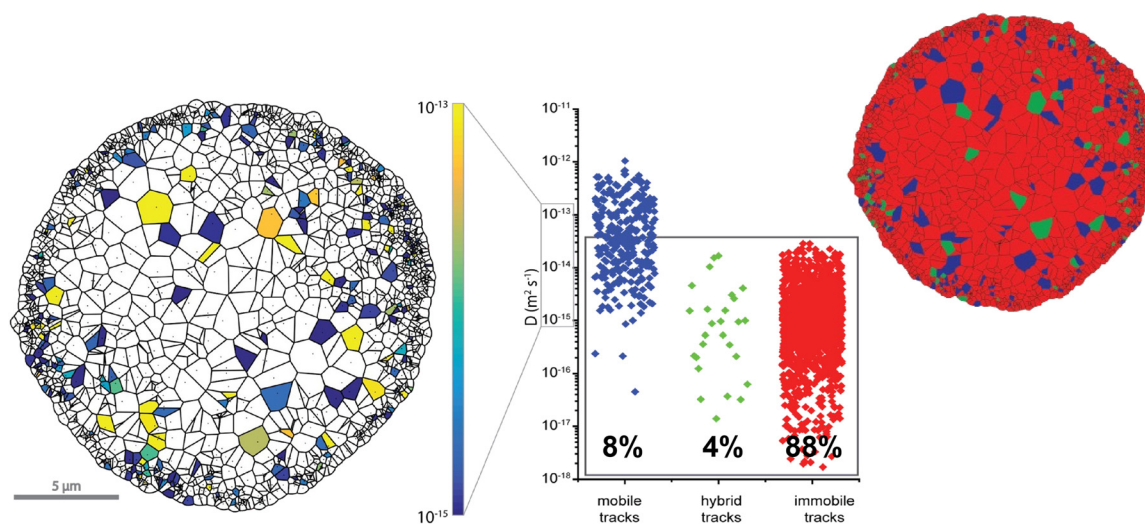


Fig. 29: Left: A Voronoi diagram showing localized diffusion coefficients in the middle cross section of the Fluid Catalytic Cracking (FCC) particle, based on the single-molecule fluorescence (SMF) microscopy experiments, outlined in Fig. 28. Each track's center of mass, indicated with a dot, is surrounded by an area that is closer to that track than to any other. The color of each area indicates the diffusion coefficient, with areas around immobile tracks being white. Right: Diffusion coefficients of each type of track of molecular motion, which we have divided in mobile, hybrid, and immobile tracks. The gray rectangle includes diffusion coefficients falling within the localization uncertainty of the single-molecule analysis. The inset Voronoi diagram (top right of the figure) shows the spatial distribution of each track type. Adapted from Hendriks *et al.*²⁴¹ with permission.

4 Theory, modeling, and simulation

As evident from the discussion above, some amount of theory and modeling is required for the analysis of any diffusivity measurement. At the simplest level, this could be application of Fick's second law with adequate boundary conditions and assuming an appropriate concentration dependence of the diffusion coefficient. Such applications of theory and modeling have been dealt with already in other sections of this report. Here, we now consider the correlation between theory, modeling, and simulation in a more general context.

Development and perfection of experimental techniques for diffusion measurement in nanoporous (notably microporous) material has significantly benefitted from a parallel refinement of the possibilities for the theoretical assessment of diffusion phenomena.^{245,246} This includes the support provided by simulations in search for hidden traps in the application of the measuring techniques, as well as to the relevance of experimental measurement in confirming the validity of theoretical predictions.

The benefit of such cross-correlations becomes immediately visible when considering, for example, diffusion in systems with nano-confinement effects, where the low diffusivities make it difficult to apply “conventional” simulation techniques (explained in Section 4.1) and the results of experimental measurement serve as a standard for the validation of the results as obtained by theoretical approaches. There are, vice versa, also numerous situations where direct experimental measurement becomes highly complicated. This occurs notably with current trends toward increasing miniaturization (see Eqs. 11 and 14), aiming at performance enhancement by a reduction of uptake and release times. In such a situation, direct measurement of the relevant parameters of mass transfer becomes increasingly difficult, enhancing the relevance of their theoretical prediction.

Both aspects of the application of theory, modeling, and simulation to diffusion in nanoporous materials apply to both micropores and meso/macropores. However, the techniques commonly applied in these two cases are quite different. Thus, Section 4.1 focuses on methods for predicting diffusion coefficients from molecular-level simulation, mostly dealing with crystalline, microporous materials, and Section 4.2 discusses aspects of (multi-scale) diffusion in meso/macroporous materials and materials with multiple levels of porosity. With increasing molecular sizes, molecular-level simulations gain importance for also mesoporous materials so that, as a matter of course, there are no fixed dividing lines between these areas.

4.1 Molecular dynamics simulation in micropores

4.1.1 Basics

In a molecular dynamics (MD) simulation, the evolution of a system of interest is followed in time, usually from an atomistic model.²⁴⁷ From the molecular trajectories of a system at equilibrium, the self-diffusion coefficient can be obtained from the Einstein equation, Eq. 6. It is also possible to obtain the Fickian and Maxwell–Stefan diffusivities from either equilibrium or non-equilibrium MD simulations.^{248,249} In MD, the trajectories are generated by propagating the system forward in time through discrete time steps, typically on the order of femtoseconds.

Simulations of tens of nanoseconds are routine with modern computers. At each time step, the forces $\vec{F}_i$ acting on each atom i of mass m_i are calculated, and the atomic positions are propagated forward in time with acceleration $\vec{a}_i$, according to Newton's equations of motion, $\vec{F}_i = m_i \vec{a}_i$, in its simplest form. Details are provided in many textbooks and review articles.^{6,247–249}

Accurate expressions for the potential energy are needed for calculating the forces. In classical MD simulations, the potential energy is typically described as a sum of terms describing bond stretching, bond angle bending, torsional potentials, and non-bonded interactions, such as dispersion, repulsion, and Coulombic forces. For adsorbates in a porous solid, the non-bonded host–guest and guest–guest dispersion and repulsion interactions are typically described by a Lennard–Jones potential between all pairs of atoms. Similarly, Coulomb interactions are calculated from partial charges placed on framework and adsorbate atoms. The accuracy of a

simulation is typically more sensitive to the accuracy of the Lennard–Jones parameters and partial charges than to the bonded interactions, such as bond stretching.

4.1.2 Best practices for MD simulations

While MD simulations can be performed for non-equilibrium systems, we focus here on simulating a system at equilibrium, since that is the most common usage of MD in nanoporous materials. A number of open-source MD codes are available, allowing researchers to perform MD without writing their own code, but it is important to understand what the code is doing, and the user must make some choices.

A first important consideration is the model or force field. These expressions for the energy and forces as a function of the atomic coordinates play a critical role in determining the results. For some well-studied systems (e.g., alkanes in MFI zeolite), well-established force fields exist. For new systems, the model should be tested against experiment. A common practice is to compare simulated thermodynamic properties such as the adsorption isotherms and heats of adsorption against experiment, since such experimental data are more commonly available than diffusion data. Agreement of the thermodynamic properties is a good starting point but may not be sufficient because at equilibrium molecules tend to sample the lower-energy configurations preferentially, but diffusion involves transitions through higher-energy configurations, such as traversing a “window” in a zeolite. Thus, it is best to have some experimental diffusion data for validation of the model. If data for the exact system of interest are not available, a related system or different temperature or loading may be enough to provide some test of the model. An increasingly attractive alternative is to use quantum mechanical calculations to develop the (classical) force field.^{250,251} In some cases, it is now feasible to replace the classical force field with forces and energies calculated from density functional theory, in the so-called *ab initio* MD.²⁵²

For crystalline materials, the (average) positions of the atoms of the framework are often available from crystallographic studies. For amorphous systems, one typically needs to generate the positions based on some prior knowledge. A critical choice in developing a model is whether to treat the framework atoms as fixed or to let these atoms move during the simulation. Simulations often start with assuming the framework is rigid, and this is often a valid assumption if the narrowest pores are large relative to the size of the adsorbates. When the pore size is small relative to the size of the adsorbate, it is essential to account for framework flexibility. It is common that zeolites and related materials can admit molecules that are nominally larger than the average crystallographic pore dimensions, and this can only be modeled with a flexible framework.

From an MD simulation, the molecular trajectories are analyzed, and the self-diffusion coefficient for species i , D_i , can be calculated from the mean-squared displacement of adsorbates over time using the Einstein relation for a system at equilibrium (i.e., without concentration gradients).

$$D_i = \frac{1}{2dN_i} \lim_{t \rightarrow \infty} \frac{d}{dt} \left(\sum_{l=1}^{N_i} \left[\vec{r}_{l,i}(t) - \vec{r}_{l,i}(0) \right]^2 \right), \quad (81)$$

where d is the dimensionality of the system, N_i is the number of adsorbates of species i , and $\vec{r}_{l,i}(t)$ is the position of molecule l of species i at time t . Also from an equilibrium MD simulation, the corrected diffusivity $D_{c,i}$ defined in Eq. 23 can be obtained from the following expression:^{6,248}

$$D_{c,i} = \frac{1}{2dN_i} \lim_{t \rightarrow \infty} \frac{d}{dt} \left(\left(\sum_{l=1}^{N_i} \left[\vec{r}_{l,i}(t) - \vec{r}_{l,i}(0) \right] \right)^2 \right). \quad (82)$$

Note that Eq. 82 does not average over all particles (as in Eq. 81) but rather tracks the collective translational motion of the molecules. Combining Eqs. 23 and 82 provides a purely equilibrium route to the transport diffusivity, D_T .

The self-diffusion coefficient D_i can be calculated from the slope of the mean-squared displacement versus time plot. Care must be taken to simulate long enough and to consider only the linear diffusive regime, where the mean-squared displacements do not reflect just the short-timescale ballistic motion. In simple terms, one needs to make sure the molecules are diffusing over the relevant length scale and not just vibrating around their initial

positions. A rule of thumb is that the molecules should move, on average, at least one unit cell during the simulation. In porous media, there also exists a sub-diffusive region that is correlated with pore wall collisions. For slit pores and fractal media, diffusion may become anomalous and the diffusivity time-dependent.^{253,254} It is recommended to graph the mean-squared displacement versus time plot to look for anomalies. The linear regime for fitting is often chosen by visual inspection, but automated approaches²⁵⁵ are helpful in removing human bias and for large-scale screening studies.²⁵⁶

Another test that an MD simulation is equilibrated is to check that the properties of the system, such as the average energies, are not changing after some initial equilibration period. Again, graphing the properties versus time is recommended. Properties of interest should be calculated from the portion of the simulation after the equilibration period, that is, when the system is, indeed, at equilibrium. Self-diffusivities calculated from MD simulations can be compared directly to experimental measurements from Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) and Quasi-Elastic Neutron Scattering (QENS).

4.1.3 Best practices in reporting results of MD simulation

Recent years have seen an increased awareness that full details should be reported in publications, so that the results can be reproduced by other researchers. For molecular simulation, this includes reporting the code used (including the specific version) and full details of the force field. Best practice is to fully tabulate all force field parameters, rather than simply referencing prior publications. A common omission is whether the so-called “tail corrections” have been applied for the Lennard–Jones potential and the associated cutoff distance. The method used for calculating the Coulombic interactions should also be reported. With the availability of supporting information and other electronic repositories, it is recommended to include (at least) sample input and output files, and this is a convenient way to report many of these details. In some cases, it may be practical to include all input and output files. Details of the MD algorithm should be reported, including the integration algorithm, the time step, any thermostats or barostats (and associated parameters), as well as the length of the simulations and how equilibration was determined.

4.1.4 Examples using MD simulations in understanding or interpreting experimental data

Understanding discrepancies between different experimentally measured diffusion coefficients: There are many examples of MD simulations providing molecular-level insights about diffusion that would have been difficult to obtain experimentally. Molecular dynamics can also play an important role in validating the diffusion coefficient values measured by different experimental techniques. Here, we discuss one prominent example. In the early 1990s when the first MD simulations in zeolites became possible, there were several well-documented systems where carefully performed measurements from PFG NMR and macroscopic methods such as ZLC yielded diffusion coefficients that differed by one or more orders of magnitude.⁵ Short alkanes in MFI (silicalite) were one such system. June *et al.* studied methane, butane, and hexane in silicalite using MD^{257–259} and found that the self-diffusivities predicted by MD agreed well with values measured by PFG NMR (and later QENS¹⁹⁸). Fig. 30 shows a comparison of the MD results with PFG NMR self-diffusivities for methane. The additional support from MD for the PFG NMR results spurred additional work to continue investigating the reasons for the discrepancy with other experimental methods.

Multicomponent diffusion: Mixtures are especially difficult to study experimentally, while they are relatively straightforward to model in MD simulations. Multicomponent diffusion simulations were instrumental in uncovering the mechanism of segregated diffusion in small-pore eight-member ring zeolites with cage-window structure.^{261,262} These materials have attracted considerable interest for separations of small molecules as membranes and adsorbents, for example, for natural gas CO₂/CH₄ separations^{263,264} and olefin/paraffin separations,^{265–267} as well as molecular sieving catalysts.²⁶⁸ It is common for mixture diffusion in the bulk and in porous materials of moderate degree of confinement that slowly diffusing molecules retard diffusion of fast molecules. However, in small-pore 8 MR zeolites, diffusion becomes segregated: CO₂ and N₂ molecules occupy window sites and hinder diffusion of methane and other hydrocarbons.^{261,262} The segregated diffusion has been confirmed by

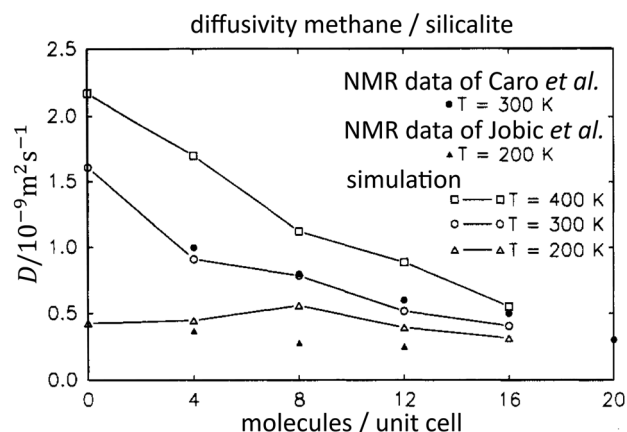


Fig. 30: Self-diffusivities for methane in silicalite calculated from MD simulations by June *et al.*,²⁵⁷ compared with PFG NMR measurements by Caro *et al.*²⁶⁰ Adapted from June *et al.*²⁵⁷ with permission.

calculating binary Onsager coefficients, and it was found that the off-diagonal components were very small compared to the diagonal components. These calculations²⁶¹ allowed the prediction of the selectivity of a DDR zeolite membrane in a good agreement with experiments.²⁶³ It is interesting that diffusivities of components in a mixture were essentially similar to single-component diffusivities over a wide range of pressures, and this was later confirmed by PFG NMR measurements.²⁶⁹

Since PFG NMR can provide self-diffusion coefficients of the individual species in a mixture, there have been several comparisons of mixture diffusivities from MD and PFG NMR.^{165,166} For example, Fernandez *et al.*¹⁶⁸ studied the effect of overall loading on self-diffusivities for mixtures of butane and 2-methylpropane (isobutane) in silicalite at 363 K. As shown in Fig. 31, both MD and PFG NMR show that the diffusivity of butane falls as the fraction of the slower-moving 2-methylpropane increases in the system (at constant total loading). The computational results are in a relatively good agreement with the PFG NMR measurements, with the largest deviation occurring at higher loadings of 2-methylpropane.

Surface barriers: Results of early PFG NMR studies¹⁷⁶ (see Section 3.11), later confirmed by advanced optical techniques such as interference microscopy^{270–273} (see Section 3.8), established that in many zeolite crystals, there is a significant mass-transfer resistance at the external crystal surface, so that the uptake rate is controlled by the combined effects of intracrystalline diffusion and surface resistance. One challenge in modeling surface barriers is that the structure of the external crystal surface is usually not known in detail. Thus, to use MD simulation, one must hypothesize a structure for the external crystal surface, and the MD simulation allows one to assess the effect on transport of the hypothesized surface. External zeolite surfaces are usually modeled with terminal silanols and may also account for pore blocking in some way. Similarly, Thomas and Subramanian modeled a variety of different external surfaces of NaY zeolite and used MD simulation of hexane to separate the contributions to the diffusivity coming from both inter- and intracrystalline regions and compared their results with those from PFG NMR.²⁷⁴ The external zeolite surface has been shown to influence adsorption selectivity in the separation of xylene isomers using BaX zeolite,²⁷⁵ and there is increasing interest in controlling crystal

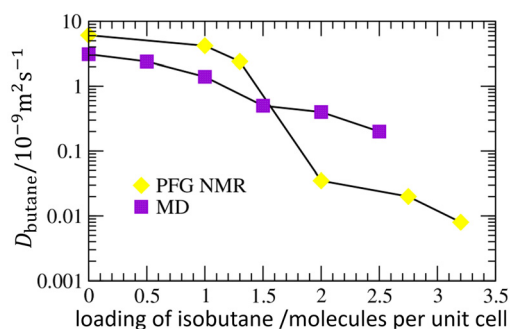


Fig. 31: Comparison of the results of MD simulation and PFG NMR measurement by Fernandez *et al.*¹⁶⁸; Self-diffusion coefficients of butane in a mixture of butane and 2-methylpropane (isobutane) in silicalite at a constant total loading of 4 molecules per unit cell at 363 K.

morphology to fine tune catalysis and separation processes.²⁷⁶ Recent advances in interference microscopy and infrared microscopy have demonstrated how transport properties may show large variations depending on the peculiarities of the different crystals within the same sample.²⁷⁷ The role of external and internal barriers to mass transfer in nanoporous materials has recently been reviewed by Xu *et al.*²⁷⁸ An overview of the techniques for their experimental measurement and the risks of misinterpretation, as often found in the literature, see, for example, the in-depth analysis of such an example in ref. ²⁷⁹, is provided in Ruthven *et al.*⁵⁵

Mesoporous, hierarchical zeolites: To understand the effect of mesoporosity on zeolite diffusion, Bai *et al.*²⁸⁰ performed MD simulations of hexane in a model system containing microporous nanosheets interspersed with mesopore channels. Surprisingly, the simulations showed that the diffusivity in these hierarchical materials can be smaller than in the corresponding purely microporous zeolite. Only at high hexane loadings or elevated temperatures, when the mesopores are sufficiently populated, does the overall diffusion in the hierarchical system exceed that in the microporous zeolite. The effect was due to the large free energy cost (mostly enthalpic) to escape from the micropores into the mesopores, and the modeled system did not include any pore blockage or surface disorder. The results allowed the authors to re-examine zero-length column chromatography data and show that these experiments are consistent with the simulation data when the crystallite size was used for the nominal diffusion length instead of the nanosheet thickness. The results underscore the complexity of diffusion in hierarchical materials, where the combination of simulation and experiment is likely to be essential in fully understanding these complex systems.

4.1.5 Applications of transition-state theory

For systems where the molecules do not move fast enough to permit the observation of diffusive behavior in an MD simulation, alternative approaches can be applied. In particular, transition-state theory (TST), in which an atomistic model (the same model used in MD) is used to estimate hopping rates between favored adsorption sites, is a useful approach. From the TST hopping rates (often corrected for possible recrossing events⁶), the diffusion coefficient can be calculated. In some simple cases, there are analytical formulas to obtain the diffusion coefficients from the hopping rates; otherwise, the hopping rates can be used as inputs to kinetic Monte Carlo simulations, which can be used to calculate the diffusion coefficients. The interested reader is referred to the literature for details and examples.^{6,248,249}

Analytical expressions based on TST can also be used to interpret experimental data. As an example, Fig. 32 displays the transport and self-diffusivities of methanol and ethanol in the MOF ZIF-8. Also shown are the corrected diffusivities, as calculated via Eq. 23 from the transport diffusivities and the shape of the adsorption isotherm. The corrected diffusivities and the self-diffusivities are found to be quite close to each other. This coincidence may be shown to be the direct consequence of transition state theory^{283–285} if molecular passages through the “window” between adjacent cages may be considered as a rare event and, in addition, to occur

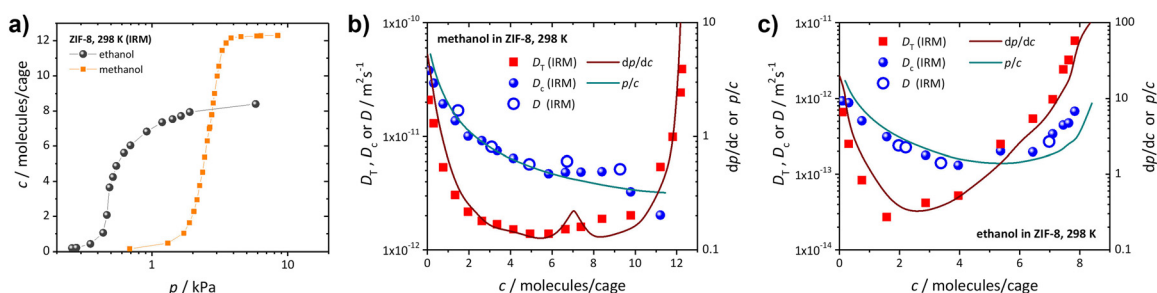


Fig. 32: Adsorption isotherm (a) and loading dependence of the transport diffusivities D_T (squares) and self-diffusivities (open circles) at 298 K for methanol (b) and ethanol (c) in MOF ZIF-8 determined by IRM (Ref. 281). The corrected diffusivities D_c (filled circles) were calculated via Eq. 23 from the transport diffusivities and the equilibrium isotherms. Full lines are the predictions of the concentration dependence of the transport and self-diffusivities following Eqs. (83) and (84). Adapted from Chmelik and Kärger (Ref. 282) with permission.

without any interaction with the remaining molecules. Under such conditions, transport and self-diffusivities can be shown to obey the relations^{109,248,282}

$$D_T = K D_0 \frac{dp}{dc} \quad (83)$$

and

$$D = K D_0 \frac{p(c)}{c} \quad (84)$$

with

$$K = \left(\frac{c}{p} \right)_{c \rightarrow 0} \equiv \left(\frac{dc}{dp} \right)_{c \rightarrow 0} \quad (85)$$

denoting the slope of the adsorption isotherm at small concentrations (Henry's law constant) and D_0 denoting the self-diffusivity in the limit of small concentrations ($c \rightarrow 0$, coinciding there with the transport diffusivity).

We recognize that, by combining Eqs. 83 and 84, the self-diffusivity automatically coincides with the corrected diffusivity as defined by Eq. 23. Moreover, the representations in Fig. 31b and c confirm the above statement that, as a rule, the concentration dependence of the corrected diffusivity (here of also the self-diffusivity) is less pronounced than that of the transport diffusivity.

4.2 Transport in mesoporous materials

4.2.1 Introduction

Modeling transport in mesoporous materials poses different challenges than diffusion in zeolites, because, unlike zeolites, most of the practically used mesoporous materials are geometrically disordered. There tends to be a distribution of pore sizes and shapes. Proper representation of the pore space to interpret experiments can thus be difficult, including the separation of morphological (pore shape and surface roughness) from topological (pore network connectivity) effects.

Effects of heterogeneity on diffusion tend to be summarized in a “tortuosity,” τ , which is used to model diffusion-limited reactions or separations in porous media. The methodology described in Section 2.2 could retrieve τ or use it as a fitting parameter, by measuring the effective diffusivity of a single species and parameterizing the equations with the molecular diffusivity and the Knudsen diffusivity. The latter depends on pore diameter, shape, length, and roughness; however, the classical expression for a smooth cylindrical infinitely long channel, Eq. 28, is almost always used.

Theoretical modeling and computer simulations of transport in pores (of different lengths, roughness, and surface properties), pore networks, and discrete particle models reveal a more complicated picture.²⁴⁸ There is no unique relationship between tortuosity and porosity. Tortuosity can be species and process dependent, for example, because the contributions of different parts of the pore space are different under reaction conditions, or when vapors condense. Does this matter in the interpretation of experiments? Here, we present an overview, distilled from Bukowski *et al.*,²⁴⁸ where we emphasize the relation between theory, simulations, and experiments.

4.2.2 Models for porous materials to relate theory and experiments

Discrete particle models consider coarse-grained particles, which are used as building blocks to construct the material. The mesopores are the negative space, the voids in between these building blocks. This representation attempts to conform to the packing, aggregation, agglomeration, fusing, or sintering of particles by which the

porous material is synthesized experimentally.^{286,287} Most commonly, the geometrical model results from a random packing that leads to overall properties in agreement with experiments, like porosity and surface area, and, possibly, a measured pore size distribution.²⁸⁸ X-ray Tomography²⁸⁹ or electron microscopy might also provide such geometrical models. An atomistic representation for the particles could be embedded into discrete particle models, which is useful in MD simulations. To simulate diffusion of fluids, molecules move through the open, accessible pore space in between the particles.

Pore network models can be constructed based on experimentally measured porosity, surface area, and pore size distribution. However, the connectivity is harder to obtain. Nitrogen adsorption and desorption measurements are the most common, accessible characterization techniques to determine the textural properties of mesoporous materials. These are volumetric methods that directly probe the pore space, rather than the particles constituting a porous material. Thus, pore network models are more widely applied than discrete particle models. Nevertheless, these shortcomings can be considerable, as the interpretation of adsorption measurements using N₂ or other probes, as well as (mercury) porosimetry, again requires a model, which involves modeling assumptions as well. The interpretation of porosimetry measurements is a mathematical “inverse problem,” thus inferring a pore size distribution and the pore connectivity is far from easy for a material with limited additional information on the pore shape.²⁸⁸ Seaton²⁹⁰ and Portsmouth and Gladden²⁹¹ have developed techniques to extract this pore connectivity from the hysteresis in nitrogen adsorption and desorption and mercury porosimetry measurements. Small-angle X-ray scattering, electron and X-ray micro- and nanotomography,²⁹² and Nuclear Magnetic Resonance^{293,294} can be used as well. For pore network reconstruction from imaging data, there is a need for upscaling from a typically small, imaged volume to larger domains. This leads to the need to construct statistically representative networks, based on the analysis of the image to extract size distributions of pores and throats and their connectivity. However, if the experimental data come from non-imaging techniques such as mercury porosimetry or gas adsorption, where not all pore space characteristics are readily available, regular pore network construction approaches are usually applied with assumed connectivity. Rigby and Chigada²⁹⁵ have used mean-field DFT²⁹⁶ to interpret data from integrated gas sorption and mercury porosimetry. The authors demonstrated that the experimental observations can be better understood in the light of mean-field DFT simulations of adsorption in representative pore models. This has led to a better description of the particular physical mechanisms underlying adsorption isotherms in disordered porous solids. In addition, the new method allows to obtain more details on the void space geometry, such as the ratio of pore neck length relative to pore body length.

Continuum models are the most used models. Solving continuum models is much quicker than solving pore network models. However, these continuum models should be correctly derived. Remarkably, most representations of mesoporous media in chemical engineering do not go much further than the work from pioneers like Wheeler in the 1950s. Effects beyond the single pore are all hidden in what Aris²⁹⁷ called a “fudge factor”: a tortuosity that includes everything from actual pore tortuosity to constrictions, reduced connectivity, roughness, and other structural effects, wrongly assuming that these effects are constant or insignificant. This is both incorrect and unnecessary. Pore size distribution and morphological information at a pore level can be included in the expression for the diffusivity, including nano-confinement effects, such as Knudsen diffusion or effects inferred from MD simulations – implying a *multiscale* simulation approach. For well-connected pore spaces that are not prone to change during operation, a continuum model, containing information from single-pore models, and with a purely network-related correction via a properly evaluated tortuosity ($\tau \leq 3$), may be sufficient. Otherwise, one of the other types of models is required.

4.2.3 Diffusion in mesoporous materials

Surface diffusion: It is difficult to isolate the contribution of surface diffusion from other transport mechanisms experimentally. Hence, it is the least well understood and characterized form of diffusion in mesoporous materials. A problem is how to experimentally differentiate between surface diffusion and bulk (molecular)

diffusion. There are many reviews on these phenomena in the literature,^{6,292,298} among others. Finding a functional form $D_s(\theta_s, T)$ of the surface diffusivity (with θ_s denoting the relative surface coverage) is not easy. If one applies, for example, the Langmuir isotherm to the Darken expression (Eq. 23), one obtains

$$D_s(\theta_s) = D_{s,0} \frac{1}{1 - \theta_s}. \quad (86)$$

This relation cannot be correct for all values of the loading, as it would imply that $D_s \rightarrow \infty$ when the maximal loading, $\theta_s = 1$, is reached. However, it is in remarkably good agreement with experimental data at least up to $\theta_s = 0.8$. Chen and Yang²⁹⁹ proposed the following, more flexible single-parameter expression that agreed well with both surface diffusion on Vycor glass with 4.6 nm mesopores (using data from Gilliland *et al.*³⁰⁰) and diffusion of various probe molecules in zeolites:

$$D_s = D_{s,0} \frac{1 - \theta_s + (\lambda/2)\theta_s(2 - \theta_s) + [H_s(1 - \lambda)](1 - \lambda)(\lambda/2)\theta_s^2}{[1 - \theta_s + (\lambda/2)\theta_s]^2}. \quad (87)$$

Here, the parameter $\lambda \geq 0$ is a measure of the blockade by other adsorbed particles and H_s is the Heaviside step function; if $\lambda = 0$, the expression reverts to Eq. 86. This is illustrated in Fig. 33.

It remains difficult to describe surface diffusion in general, let alone unify this model with a theory for diffusion in zeolites, given the wide variety of interactions of molecules with heterogeneous surfaces. Both on surfaces and in zeolites, the diffusivity can level off or show a maximum as a function of loading, θ_s . A case in point was presented by Valiullin *et al.*,²⁹⁴ where PFG NMR diffusion and NMR adsorption data of acetone in mesoporous silicon with pores of 4 nm showed that the surface diffusivity first increases with loading but then levels off at higher loadings, contrary to Fig. 33. For a sample with pores of 10 nm, a maximum was found. A diffusion model that included surface heterogeneity and a generalized Freundlich adsorption isotherm showed a good agreement with experiments.

Knudsen diffusion: Ruthven *et al.*³⁰¹ have carried out a detailed analysis of their experimental permeance data for several gases (He, Ar, N₂, CH₄, and C₃H₈) in a mesoporous silica membrane, where they found that the experimental diffusivities are proportional to $(T/M)^{0.5}$, in conformity with Knudsen's model, Eq. 28 (Fig. 34). No

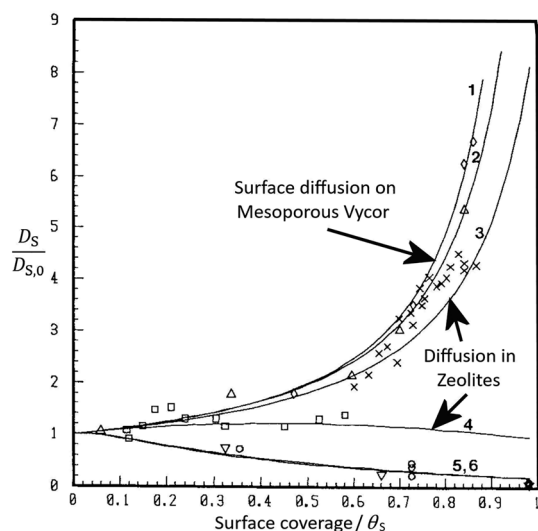


Fig. 33: Unified modeling of surface diffusion on mesoporous materials (here, SO₂ on Vycor glass at 15 °C, line 1; $\lambda = 0$) and diffusion in zeolites (other lines, $\lambda > 0$), using Eq. 87. The experimental data for zeolites correspond to ethane on 4 Å at 50 °C (line 2), propane on 5 Å at 50 °C (line 3), benzene on ZSM-5 at 65 °C (line 4), and triethylamine on 13X at 190 °C (line 5) and 160 °C (line 6). Adapted from Chen and Yang (Ref. 299) with permission.

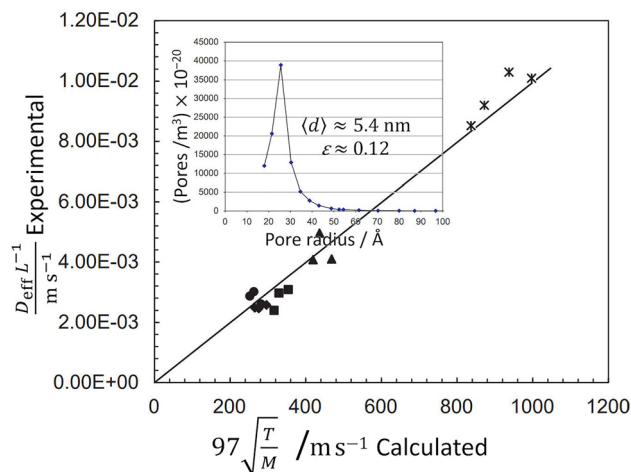


Fig. 34: Experimental measurements of the effective diffusivity in a mesoporous silica membrane, D_{eff} , normalized by the active layer thickness, L , as a function of Knudsen's theoretical prediction for the dependence on temperature and molecular mass, $D_K \sim (T/M)^{0.5}$ with T in Kelvin. The narrow pore size distribution of the membrane is shown in the inset. Adapted from Ruthven *et al.*³⁰¹ with permission.

obvious difference in behavior was found between the lighter and heavier species (Ar and C_3H_8). They concluded that, even under conditions of significant adsorption, the simple Knudsen model still provides a good representation of the permeance data. Of course, for porous media (as opposed to single channels), one must know the network tortuosity to obtain quantitative agreement.

Very recently, Besser *et al.*³⁰² carried out experiments of Knudsen diffusion of a wide range of gases (like those by Ruthven *et al.*,³⁰¹ plus CO , CO_2 , Ne, and C_2H_4) in carefully synthesized membranes with a monomodal pore size distribution (23, 33, and 60 nm pore diameter), grafted with functional groups of broadly varied type and length. Knudsen's formula, in particular the proportionality to $(T/M)^{0.5}$ and to the pore diameter, was confirmed. Surface diffusion did not play a significant role. Remarkably, the type of functional groups had no effect on the results, only the length of those groups. Non-binding interactions, similar to steric hindrance, but originating from a “quasi-liquid” layer at the pore walls, resulted in the scattering that is at the basis of classical Knudsen diffusion and the observed decrease in membrane flow. Thus, they found that the origin of the heterogeneity of the pore walls (geometric or chemical) causing delayed molecular retention and diffuse scattering is irrelevant, which they stated to agree with the theoretical findings of Coppens and Dammers.²⁸⁶

Diffusion in mesopores is clearly a complex phenomenon with confinement effects that are theoretically still not fully understood. Careful experiments on tailored materials are required to investigate and properly account for surface heterogeneity, whatever its origin. This has become possible with the advent of nanostructured mesoporous materials.

4.2.4 Effects of the surface morphology

Many amorphous, mesoporous materials have a fractal internal surface. A fractal dimension, D_f , can be associated to the roughness and experimentally measured. For smooth surfaces, $D_f = 2$, while $D_f = 3$ for surfaces that are so convoluted that they are space filling. For many amorphous mesoporous materials, the fractal dimension of the surface is somewhere in between: $2 < D_f < 3$.

This was confirmed by many experimental studies,^{303,304} using adsorption measurements and small-angle X-ray scattering. The surface roughness that is inherent to amorphous materials can be accounted for in studies of

diffusion and reaction in mesopores.³⁰³ Using the principles of fractal geometry, the effects of roughness on diffusivities and reaction rates, and therefore also on conversions and product distributions, can be calculated. Especially when Knudsen diffusion in mesopores plays a controlling role, the effect of the fractal surface roughness proves to be significant. This theoretical and computational work should prompt experimental investigations to directly evidence effects of fractal surface roughness on diffusion in mesopores, an effect that is obscured by the pore network topology, which complicates interpretations and lumps various effects in the “tortuosity.”

Another factor is slip, which has also been invoked to explain high fluxes observed for water flowing through carbon nanotubes, following the experimental observations by Majumder *et al.*³⁰⁵ For nitrogen transport through multi-walled carbon nanotube (CNT) membranes, Hinds *et al.*³⁰⁶ obtained an excellent agreement with regular Knudsen diffusion; functionalization of the tubes further reduces transport. Striolo³⁰⁷ found through molecular simulations that a few defects in a CNT would suffice to considerably drop the high flux predictions for water flowing through them and lose the effect of a high slip rate.

4.2.5 Effects of the pore network topology

Nano-confinement effects can be studied fundamentally on single channels, but, typically, comparison with experiments requires a pore network. Thus, the question that concerns us here is: When are topological, network effects noted? Is there an effect of the presence of reaction on the effective diffusivity or, alternatively, tortuosity?

Zhang and Seaton³⁰⁸ have found that the effective diffusivity used in the continuum diffusion–reaction model, when defined appropriately, does not depend on the reaction rate. This conclusion applies only to catalysis with monodisperse structures and to microparticles within bidisperse, hierarchical catalysts. Hollewand and Gladden³⁰⁹ also warned about the importance of accounting for the hierarchical structure, rather than randomly distributing a bimodal pore size distribution over a pore network of defined connectivity.

Burganos and Sotirchos³¹⁰ proposed a general methodology to estimate the effective diffusivity of a pore network with arbitrary pore size distribution using the effective medium theory of approximation (EMA), in combination with the smooth field approximation (SFA). Despite the clear advantages offered by pore network models, they rely on parameters regarding the pore network topology that might not be readily available. Thus, it is comforting to know that a comparison of numerical simulations via continuum and pore network models by Zhang and Seaton³⁰⁸ showed that the effective diffusivity was generally independent of the reaction conditions and a continuum model could be used, except close to the percolation threshold (e.g., due to deactivation or otherwise severely hindered transport, as shown by, e.g., Ye *et al.*³¹¹) or if the transport limitations are so significant that concentrations drop appreciably over a few pore lengths from the particle surface (including the surface of the particles within a pellet, for hierarchically structured porous media).

This means that, barring the just cited exceptions or if an explicit pore network topology is known from tomographic imaging and other reliable experimental techniques, a continuum modeling approach suffices for single-phase diffusion and reaction problems. This model should, however, properly include confinement effects induced by the material’s morphology and surface properties, as discussed earlier. For partially condensing vapors and gas–liquid reaction systems, pore network effects might again occur, due to capillary phenomena and partial flooding; these could even result in hysteresis effects, with different rates for increasing or decreasing process variables, like the temperature or pressure, as discussed by Ye *et al.*³¹²

4.2.6 Multi-component diffusion

The derivations of the dusty-gas model (DGM) are complex,³¹³ but the results are startlingly simple, as they formally look like the Maxwell–Stefan equations, with an additional Knudsen diffusion flux, and effective

transport parameters. Further simplification to a Fickian description, however, is rarely allowed. Indeed, in 1963 already, Rothfeld³¹⁴ showed that even for binary gas mixtures with non-equimolar counter-diffusion, the effective diffusivities in a porous medium depend on the local mole fraction, and a ratio of position-dependent molar fluxes (arising from the Maxwell–Stefan or DGM description) must be included in the equations, so that the effective diffusivities are also position dependent. Only then could an excellent agreement with experiments be obtained. This greatly affects observed membrane permeabilities and catalytic reaction rates. Even though more than half a century has passed, this is still largely ignored! There is no reason for this, with our current computer capabilities: the full Maxwell–Stefan equations can and should always be used,³⁰³ barring situations with single components or equimolar counter-diffusion.

4.2.7 What should be done to relate experiments to theoretical interpretation?

More realistic representations of mesoporous materials can be obtained, thanks to tomographic imaging; however, even the most advanced electron and nano-X-ray tomographic tools are still unable to visualize amorphous materials at a resolution better than a few nanometers, and then only on a very small sample – thus typically ignoring surface roughness, and assuming macroscopic homogeneity and isotropy to extrapolate results. This calls for a merger of imaging with atomistic information and statistical modeling, aided by a combination of experimental techniques (porosimetry, scattering, etc.).

Multiscale representations of amorphous materials are becoming possible, suitably integrated with pore network and morphological statistical representations that are parameterized on the basis of advanced material characterization methods. In addition, synthesis-mimicking simulations can support efforts to accurately represent mesoporous materials. Fully atomistic material representations are hard (or currently impossible) to achieve. But this is not necessary. One can combine statistical information, consistent with measurable quantities, such as pore volumes, (sub-) particle and pore size distribution, surface area, and even pore shape and connectivity – parameters hard to obtain a decade or more ago. Discrete particle models could be used, and pore networks could be derived from them, with “decorated” walls, informed by imaging, porosimetry, and spectroscopy. Then, we advise to revisit those fundamental theoretical insights and approaches, with suitable modifications to include molecular-scale information (nature of the interactions between molecules, and between molecules and the walls). Such an approach would combine molecular dynamics simulations within representative sections of the material (not only single pores but also porous “voxels” or cells) with Monte Carlo simulations, pore network models, statistical volume averaging techniques, or simple continuum models to scale up results from the nanoscale to the particle scale. For bimodal pore size distributions, the next level is again treated with a continuum or discrete modeling technique, depending on the degree of heterogeneity. Even macroscopic heterogeneity can be included in such a multiscale modeling approach.

4.2.8 Diffusion in materials including zeolites, with multiple levels of porosity: an example

The beneficial effects of introducing mesopores on zeolite mass transfer have been demonstrated by Christensen *et al.*,³¹⁵ using meso-/microporous ZSM-5 for the alkylation of benzene with ethene. This is a suitable test reaction, due to its relative simplicity, with a lot of available experimental and computational information, in addition to its large-scale industrial application, where diffusion limitations are present. Hansen *et al.*³¹⁶ used a combination of quantum chemical simulations, molecular simulations (Monte Carlo, MD) and a continuum approach to simulate the ethylation of benzene over H-ZSM-5 particles. In that study, Maxwell–Stefan equations in combination with ideal adsorbed solution theory (IAST) were employed, whereby as many data as possible have been obtained from quantum chemical (reaction rates) and molecular simulations (adsorption isotherms and diffusivities) to make the model predictive.

Integrating the microscopic simulation results from this work in a multiscale simulation of the ethylation of benzene in a catalytic reactor, Rao *et al.*³¹⁷ optimized the structure of macro/meso/microporous pellets, consisting of a composite of H-ZSM-5 and mesoporous silica. They determined the zeolite fraction that would minimize the effects of transport limitations on the pellet and the reactor level. Excellent agreement with reactor-scale experiments was found, but only when surface barriers across the external surface of the H-ZSM-5 crystals were accounted for, showing for the first time the importance of such barriers in practical processes.

As an alternative approach, in Schneider *et al.*³¹⁸ and Hwang *et al.*³¹⁹ mass transfer in meso-/micro-porous host systems is quantitated within the frame of the two-region model^{142,144} by introducing a set of four parameters, including the diffusivities in the two pore spaces, their exchange rate, and the relative occupation numbers.²⁴⁸ If the diffusion coefficients in the mesopores are sufficiently large (the case aimed for in practice), in the relationships of two-region diffusion their occupation probability only appears as a prefactor before the mesopore diffusion coefficient, reducing the number of free parameters to three.

In summary, to create meaningful hierarchical models, it is necessary for theoreticians and experimentalists to collaborate, especially for characterization and model generation.

5 Conclusions

The propagation of guest molecules within a nanoporous host material as a result of their random thermal motion—in short, molecular diffusion—is a complex phenomenon. Quantifying molecular diffusion in such porous materials is a correspondingly complicated, but also rewarding, task. In addition to temperature and guest concentration, the rate of diffusion is clearly a function of the molecules under consideration and of the distance of observation. It is, notably, their sensitivity with reference to this latter item in which—together with the specifics of the measuring process—the various analytical techniques of measurement differ from each other. As a result, different measurement techniques may yield completely different results despite being applied to one and the same host–guest system. The situation is further complicated by the fact that the materials themselves are often very fragile and can undergo structural changes during preparation for a specific analytical measurement. There is, in addition, the possibility of misinterpretation of the primary data provided by the measurement. This is a particular risk whenever changes in the host–guest system caused by the diffusion process, such as its mass during molecular uptake or release, are observed rather than the diffusion process itself.

In this context, the multitude of different measurement techniques that we have at our disposal (and whose number will probably continue to increase, stimulated by the development of new measurement principles and new types of nanoporous materials) is a great fortune. This is particularly important on elucidating the rate-determining steps by following the diffusion process over widely varying diffusion path lengths. Furthermore, some of the “indirect” methods offer relatively quick access to important information on molecular mass transfer without extreme expenses for specific pieces of analytical equipment.

The actual task is, therefore, to select the most suitable measurement techniques for the respective purpose from the spectrum of available analytical tools and to apply them correctly. Ideally, this should be done in the context of other analytical methods, both to confirm one’s own conclusions and to augment the description of a porous material to properly describe the overall process of mass transfer. Hence, a multipronged approach to elucidate molecular diffusion is recommended. With a problem-related inclusion of fundamental relations of diffusion theory and the opportunities offered by modeling and simulation, this integration process can be significantly promoted to bring a lot of new insights not only in terms of molecular diffusion of the guest molecules but also about the pore structure and connectivity of the host material.

By providing guidelines for the measurement and reporting of diffusion properties of chemical compounds in nanopores, the present treatise strives to contribute to the clarification and standardization of the presentation, nomenclature, and methodology associated with the documentation of diffusion phenomena in nanoporous materials. This purpose is served by the following summary presentations of the individual measurement techniques as well as by a list of the symbols, corresponding to the recommended nomenclature, and a list of the used abbreviations.

6 Summary with tables for the characterization of various experimental techniques and the used symbols and abbreviations

Experimental techniques applied for the study of guest diffusion in nanoporous host materials are usually classified with regard to two aspects: first, whether the measurements are performed under typically equilibrium or non-equilibrium conditions (i.e., in the presence of a concentration gradient), and second, with regard to the diffusion pathways traveled by the molecules during the measurement.^{246,320} Regarding this second criterion, measurement techniques are therefore referred to as macroscopic (measurement with/of diffusion paths through beds of crystals/particles), mesoscopic (measurement with a single crystal/particle without spatial resolution), microscopic (diffusion paths within a single crystal/particle), or sub-microscopic (focusing mainly on the diffusion steps). Given the main fields of their application, the measuring techniques presented in this report are thus commonly classified as shown in Table 1.^{246,320} The length scale covered by the guest molecules during measurement by the various measurement methods is clearly a function of the crystal/particle sizes of the sample under study.

It has to be mentioned that the given classification cannot be more than a general guide. Techniques sometimes deviating from the given assessment include Quasi-Elastic Neutron Scattering which, under favorable conditions, allows the recording of displacements into the range of nanometers (making it a “microscopic technique”), and PFG NMR which, for sufficiently large observation times, is also applicable for macroscopic diffusion measurement. If performed with only a small amount of adsorbent particles, the information attained by some of the techniques mentioned top right may be referred to as meso- rather than macroscopic. It is also worth mentioning that the equilibrium techniques may also be applied under non-equilibrium conditions and that, by the application of suitably chosen isotope mixtures, the non-

Table 1: Experimental techniques applied for the investigation of guest diffusion in nanoporous host–guest systems dealt with in this report, classified with reference to the scale of observation (“Microscopic vs. Macroscopic”) and the conditions, under which the measurements are (generally) performed (“Equilibrium vs. Non-Equilibrium”). The numbers in parenthesis refer to the respective sections.

Measurement Scale	Measurement Method	
	Equilibrium	Non-Equilibrium
Macroscopic		Uptake/Release measurement (3.3) Zero length column (ZLC) technique (3.4) Adsorption column dynamics (3.5) Frequency response (FR) technique (3.6) X-ray computed tomography imaging (3.9) Nuclear Magnetic Resonance Imaging (MRI, 3.10) (Single-crystal) membrane permeation (3.7)
Mesoscopic		
Microscopic	Pulsed field gradient (PFG) nuclear magnetic resonance (3.11) Single-molecule tracking (SMT, 3.14)	Microimaging (3.8)
Submicroscopic	Quasi-Elastic neutron scattering (QENS, 3.12) Solid-state nuclear magnetic resonance (3.13)	

equilibrium techniques may as well be applied for studying diffusion under equilibrium conditions, that is, for the measurement of self-diffusivities.

There is a wealth of further properties that can be used to characterize the predictive capabilities of diffusion measurement techniques. One of them refers to the potential of a given measuring technique for providing selective information about the diffusivity of a single component within a mixture. In fact, in most cases of their practical application, nanoporous materials are contacted by mixtures rather than by a single component and it is the behavior of the individual components of the mixture that is mainly of interest. While in some techniques, including single-particle tracking and microimaging via IR microscopy, the selectivity toward a certain molecular species is inherent to the technique, with other techniques the selective measurement of diffusivities is only possible with extreme additional effort or sometimes not at all. Furthermore, it makes a big difference whether a measuring technique is applicable only to a bed of crystals, like PFG NMR or common measurement of the adsorption/desorption kinetics, or whether it may be applied to a single crystal. Therefore, the means of confirming the correctness of the obtained conclusions in each of the individual methods are correspondingly different. The following tables provide a summary of all these aspects for the measurement techniques presented. In this way, they also serve as a brief introduction to each of them (Tables 2–4).

Table 2: Specification of the experimental techniques applied for the measurement of diffusivities in nanoporous host–guest systems dealt with in this report.

Uptake and Release Measurement (see Section 3.3)

Principle of measurement

- Measurement of the time dependence of molecular uptake or release by a nanoporous crystal/particle, following a variation of the pressure in the surrounding atmosphere.
- Determination of the intrinsic diffusion time by comparison with (i.e., fitting to) the corresponding solution of Fick's 2nd law (Eq. 7), with the diffusion time (and—in the presence of surface barriers—with the surface permeability) as free parameter(s).

Accessible information and conditions of measurement

- Primary data: uptake/release times.
- Measurement of transport diffusion in general, of self-diffusion by recording tracer exchange.
- Sorbent needed: Typically tens of milligrams.
- Observation times: From tens of seconds with upper limit determined by signal stability.
- Covered space scales: Given by the extension of the crystals/particles under study.

Strengths

- Measuring equipment (e.g., in gravimetric and volumetric measurements) easy to access.
- A large variety in the options of measurement (including mass spectrometry and the measurement of nuclear radiation by the use of radioactive isotopes) allows diffusion measurement also under multicomponent adsorption.

Weaknesses and traps

- Molecular uptake and release are accompanied by a number of processes acting in addition to diffusion that may as well affect the overall time constant, notably including the exchange of the heat of sorption with the surroundings and transport resistances in the bed of crystals/particles and on their surface. Ignoring them can lead to significant errors in the resulting diffusion times.
- Diffusivities are, quite generally, a function of the given loading, which has to be taken account of by measurements with large pressure steps, where the covered loadings must be expected to give rise to a notable variation in the local diffusivities during the experiment.
- Additional complications due to possible spreading in crystal/particle size, diffusivity, and surface permeability, providing quite a number of “free” parameters that might give rise to an incorrect fitting.

Tests of consistency

Measurement

- With varying amounts of adsorbent, ideally dispersing the material in different ways.
 - Over different pressure steps.
 - Of both ad- and desorption over the same pressure interval to identify if the system is linear.
 - With addition of inert metal material to check for heat effects, if possible repeat experiments with different particle sizes.
-

Table 2: (continued)

Zero-Length Column (ZLC, see Section 3.4)**Principle of measurement**

- As a preparatory step, the sample is equilibrated with the guest molecules contained in a carrier gas at, in general, low concentration (“Henry region”). Measurement of transport diffusion time (close to zero loading) by stopping the influx of the guest molecules, plotting the time dependence of their concentration at the column outlet, and fitting to the time dependence as obtained from the solution of Fick’s 2nd law (Eq. 7) for the given initial and boundary conditions.
- Measurement of self-diffusion is possible, but now by switching the guest input to a tracer (i.e., an isotope), with the option of measurement at also higher loadings.

Accessible information and conditions of measurement

- Primary data: uptake/release times.
- Measurement of the coefficients of transport diffusion at low loadings and of self-diffusion by recording tracer exchange.
- Sorbent needed: Typically milligrams.
- Observation times: From seconds up to around 20 h.
- Covered space scales: Given by the extension of the crystals/particles under study.

Strengths

- Straightforward (and in general inexpensive) experimental arrangement.
- Essentially isothermal.
- “Partial loading” (PL) experiments (i.e., the observation of desorption before equilibration) provide a straightforward means to distinguish between limitation by diffusion, surface barriers, or their combination.
- Zero length column (ZLC) may as well be applied for the measurement of sorption isotherms (namely, for flow rates sufficiently small in comparison with the intercrystalline exchange rates).
- Varying carrier gas provides a simple means to identify macropore diffusion resistances.
- A concentration-vs- Ft (product of the volumetric flowrate and time, or “eluted volume”) plot provides a simple means to check for kinetic control and consistency of experimental curves.

Weaknesses and traps

- Interpretation of the results using a linear model without realizing that the system is nonlinear and under equilibrium control.
- Complications due to possible spreading in crystal/particle size, diffusivity, and surface permeability, providing quite a number of “free” parameters that might give rise to an incorrect fitting.

Tests of consistency**Measurement**

- With different carrier gases.
- With different flow rates of the carrier gas and Ft plot to check data consistency.
- At least one partial loading experiment.
- Repeat at different concentrations.
- If possible repeat experiments with different particle sizes.

Adsorption Column Dynamics (see Section 3.5)**Principle of measurement**

- The sample is equilibrated either with a pure inert carrier or with the guest molecules contained in a carrier gas. Measurement of transport diffusion time by changing the inlet concentration and fitting the resulting exit concentration to solution of the detailed column model. Measurement of self-diffusivities is possible, but now by switching the guest input to a tracer (i.e., an isotope).
- Alternatively, a concentration pulse is added at the inlet and the resulting response is monitored at the outlet (chromatographic peak).

Accessible information and conditions of measurement

- Primary data: uptake/release times.
- Measurement of transport diffusion time and of self-diffusivities by recording tracer exchange.
- Sorbent needed: Typically tens of milligrams to kilograms.
- Observation times: From tens of seconds to several hours.
- Covered space scales: Given by the extension of the crystals/particles under study.

Strengths

- Straightforward (and in general inexpensive) experimental arrangement.
- Varying carrier gas provides a simple means to identify macropore diffusion resistances.
- Adsorption and desorption runs allow to check for linearity.
- Easily extended to multicomponent systems.
- Measures average properties of large batches.

Weaknesses and traps

- Requires complex model (non-isothermal and nonlinear) unless experiments are purposely designed to run close to isothermal and linear conditions.
- General model is influenced by at least axial dispersion, heat transfer mechanisms, and pressure drops (especially for powdered materials), resulting in a potentially large uncertainty on the resulting diffusion time.

Table 2: (continued)

-
- Additional complications due to possible spreading in crystal/particle size, diffusivity, and surface permeability, providing quite a number of “free” parameters that might give rise to an incorrect fitting.
 - May be difficult to separate contributions from intracrystalline diffusion and surface resistances.

Tests of consistency

- Perform experiments at high enough flowrates to ensure kinetic control (under linear conditions show that the HETP increases with flowrate).
 - Determine diffusion times using the experimental mean residence time to normalize time.
 - Run at least three different flowrates in both adsorption and desorption.
 - Change carrier gas.
 - Measure the temperature ideally in two positions along the column.
 - Measure pressure drop.
 - If possible repeat experiments with different particle sizes.
-

Frequency Response (FR, see Section 3.6)**Principle of measurement**

A variable (e.g., volume/pressure, or pressure/concentration for in-flow variant) of the host–guest system is perturbed periodically around an equilibrium state. The resulting periodic response in another variable (e.g., pressure or concentration) is measured. System parameters like diffusion time or surface permeability are determined by fitting to the corresponding solution of Fick’s 2nd law (Eq. 7).

Accessible information and conditions of measurement

- Primary data: uptake/release times.
- Measurement of transport diffusion, preferably with small perturbations ensuring linearity of the underlying relations.
- Sorbent needed: Typically tens of milligrams for CSFR and grams for PSFR/VSFR.
- Observation times, corresponding with the reciprocal frequency. Up to 100 Hz for closed systems and 1 Hz for flow systems.
- Covered space scales: Given by the extension of the crystals/particles under study.

Strengths

- Observation with varying frequencies introduces an additional degree of freedom in the experimental parameters, which greatly increases the reliability in assigning the observed dependencies to their underlying mechanisms (e.g., intracrystalline diffusion or surface permeation).
- Minimizing the risk of measuring errors as a periodic process without dependence on the initial conditions.
- Recognizing heat effects due to its sensitivity to different resistances through frequency spectrum.
- By applying small perturbation to ensure linearity of underlying relations, FR allows study of concentration dependence of transport diffusivities.

Weaknesses and traps

- Risk of unrecognized influence of bed diffusion since micropore- and macropore-dominated diffusion resistances give rise to the same shape of the response curve.
- Time-consuming measurement due to cyclic modulation over a broad range of frequencies.
- Additional complications due to possible spreading in crystal/particle size, diffusivity, and surface permeability, providing quite a number of “free” parameters that might give rise to an incorrect fitting.
- Unidentified signal latency may hamper part of the analysis allowing only to consider amplitude ratios.

Tests of consistency

- Measurement with varying amount/arrangement of sorbent.
 - For FR curves exhibiting bimodal behavior, consider conducting additional experiments with the adsorbent intimately mixed with inert metal balls. This approach helps to differentiate heat transfer effect from mass transfer effect.
 - If possible repeat experiments with variations in particle or crystal size, which allows for the differentiation between micropore and macropore diffusion.
-

Membrane Permeation (see Section 3.7)**Principle of measurement****Non-stationary:**

- Pressure transient response in the permeate side of a crystal densely embedded into an impermeable (e.g., epoxy or metal) film or a dense nanoporous layer. The data are plotted to obtain the time-lag (or the diffusion time), which is related through Fick’s 1st law (Eq. 1) to the transport diffusivity, based on knowledge of the extension of the crystal in flux direction (the layer thickness).

Stationary:

- An overall mass balance is applied to obtain the flux through the membrane from measured inlet and outlet component flowrates on both sides of the membrane. The flux is related to the product of the equilibrium constant and the transport diffusivity.

Table 2: (continued)

Accessible information and conditions of measurement**Non-stationary:****Primary data:** time-lag

- Measurement of transport diffusivities.
- Sorbent needed: One large single crystal (suitable for being densely embedded in an impermeable film) or a dense layer of nanoporous material (on a macroscopic support).
- Observation times: From seconds to several hours corresponding to at least the diffusion time.
- Covered space scales: Given by the extension of the crystals/particles under study.

Stationary:**Primary data:** molar flux through membrane

- Measurement of transport diffusivities in general but can also be applied to tracer exchange.
- Sorbent needed: One large single crystal (suitable for being densely embedded in an impermeable film) or a dense layer of nanoporous material (on a macroscopic support).
- Observation times: From seconds to several hours corresponding to at least the diffusion time. This is determined from the evolution of the measured signals.
- Covered space scales: Given by the extension of the crystals/particles under study.

Strengths

- Direct measurement of molecular fluxes as the quantity of immediate interest in many applications.
- Applicable to diffusivity measurement in multicomponent systems by, for example, mass spectrometry.
- Fluxes of different components are simultaneously recorded.
- As the measurement is a combination of adsorption and desorption it is close to isothermal.

Weaknesses and traps

- The preparatory steps in fabricating either type of membranes are highly challenging.
- Leaks and the possibility of their sudden occurrence are a constant danger.
- The influence of transport barriers at the crystal surface (and, in the nanoporous crystal layers, thus also in their interior) can cause an additional reduction of the flow rate which generally remains undetected, leading to an underestimation of the diffusion coefficient.
- As an overall transport resistance is measured, the support may become limiting for fast-diffusing and strongly adsorbed components.
- Due to repeated sample activation, the stability of the membrane material and/or the interface between the microporous material and the support may become an issue.

Tests of consistency

- Check for external leaks.
- Check membrane tightness by measurement with molecules with sizes notably exceeding the pore sizes of the crystals/particles under study. Any permeation of such molecules through the tested membrane indicates defects in its tightness.
- Perform experiments with different pressure steps/differences.
- Ensure that the time-lag analysis is applied to the linear regime or use full solution.
- Ensure pressure balancing in Wicke–Kallenbach type systems.
- Use nonlinear models for systems with large pressure steps.
- For multicomponent systems, it is important to measure the flowrates on both sides of the membrane and to use an appropriate model, for example, Maxwell–Stefan, to take into account also counter-diffusion and concentration polarization effects.

Microimaging (by IFM and IRM, see Section 3.8)**Principle of measurement**

- Application of interference microscopy (IFM) or IR microscopy (IRM) for recording guest distribution (more precisely: The concentration integral in observation direction) within a given crystal/particle. This information coincides with that on local concentrations in one- and two-dimensional pore systems perpendicular to observation direction and with three-dimensional pore systems with top and bottom faces, perpendicular to observation direction, impermeable for guest molecules.
- Diffusivities and surface permeabilities may be determined either by application of the defining equations, Fick's 1st law, Eq. (1), and Eq. (9), or by fitting of the evolution of the measured profiles to the corresponding solution of Fick's 2nd law

Accessible information and conditions of measurement

- Primary data: evolution of guest concentration within a given crystal/particle if applied “microscopically” (i.e., when applied to studying transient concentration profiles within the crystal/particle) or uptake and release curves (notably their time constants) when applied “mesoscopically” (on recording overall loading without spatial resolution).
- Sorbent needed: One sufficiently large single crystal/particle.
- Sizes typically needed for microscopic measurement by IFM: larger than 10 μm , by IRM: larger than 30 μm .
- Time resolution: seconds (IFM), tens of seconds (IRM).
- Observation times: Essentially no upper limit.
- Covered space scales (i.e., spatial resolution): Attainable values in favorable cases around, respectively, 1 μm (IFM) and 3 μm (IRM).

Table 2: (continued)

Strengths

- Recording of the evolution of concentration profiles in the crystal/particle interior, as known so far mainly only as the solution of the corresponding differential equations in standard textbooks.
- Straightforward application to also multicomponent diffusion measurement via IRM by using the IR signals of the different components as their finger prints.
- *In situ* observation and recording of the evolution of the distribution of the various components involved in a chemical reaction within a nanoporous catalyst via IRM.
- Most direct determination of surface resistances via their defining Eq. (9) by simultaneous measurement of the incoming or outgoing guest fluxes and of the given (instantaneous) boundary concentrations.

Weaknesses and traps

- Primary information is on the concentration integral in observation direction rather than on local concentrations.
- Operation with and activation of single crystals/particles inside the cuvette of the microscope are severely restricted and only possible in a limited pressure and temperature range.
- The severe constraints on their activation and the relatively large internal surface area compared to the sorbent capacity make measurements very susceptible to impurities, that is, to deposits on the external surface and inside giving rise to additional transport resistances.
- Transparency of the host material as a prerequisite.

Tests of consistency

- Demonstration of the reproducibility of results when measuring with different crystals/particles of the same species to exclude possible artifacts caused by contamination and/or degradation.

X-Ray Computed Tomography (CT) Imaging (see Section 3.9)**Principle of measurement**

- Recording of the spatial distribution of the attenuation of an X-ray on passing the object (here a column packed with pelleted nanoporous material permeated by the guest molecules under study), commonly presented as 2D cross-sectional maps of attenuation coefficients (tomogram) that represent a slice of the imaged object. The complete 3D image is obtained by their stacking together.
- If the measurement is carried out as a breakthrough experiment, the same principles as discussed for Section 3.5 apply. If the measurements are similar to volumetric experiments, then Section 3.3 applies.

Accessible information and conditions of measurement

- Primary data: maps of X-ray attenuation put together to 3D images allowing the observation of molecular uptake on (release from) individual pellets with diffusion times obtained from the fit of the appropriate diffusion equation under nonlinear and non-isothermal conditions.
- Sorbent needed: Typically tens of grams for column filling.
- Time resolution of seconds, spatial resolution of around 0.01 to 0.05 mm² (in cross-sectional extension) and 0.5 to 1 mm (in longitudinal extension), with voxel volumes (under ideal conditions) down to 0.1 mm³.

Strengths

- Spatially resolved observation of the filling/emptying of macroscopic nanoporous objects, including beds of pellets or crystals/particles.
- Observation of the filling/emptying of the individual pellets within a column.

Weaknesses and traps

- Direct measurement of intracrystalline/intraparticle diffusion only with extremely large crystals/particles (range of millimeters).
- Need relatively large sample sizes, with the corresponding difficulties in avoiding intrusion of bed and heat effects.
- When used as on recording ACD (adsorption column dynamics, Section 3.5, now with focus on gas concentration inside the column rather than at the outlet), subject to the same weaknesses necessitating, for example, the application of a detailed model that includes heat and mass transfer in the column.

Tests of consistency

- Confirming the validity of the thus obtained intracrystalline/intraparticle diffusivities by checking the required (square-size dependence, Eq. 11) dependence of the uptake/release time on the crystal/particle size.
- Ensuring system is not under equilibrium control.

NMR Imaging (see Section 3.10)**Principle of measurement**

- The frequency of an NMR signal is determined by the externally applied magnetic field (its “magnetic flux density”). Thus, by measurement with well-defined field gradients, the location of the nuclear spins (and, hence, of the associated molecules) becomes accessible by analysis of the frequency dependence of their (NMR) signal. Suitably chosen sequences of field gradients with varying orientation allow the 3D determination of molecular distribution.
- More complex programs may provide more information, including molecular diffusivities (as considered in Section 3.11) and nuclear magnetic relaxation times (reflecting molecular interaction with the surrounding).
- If the transport measurement is carried out as a breakthrough experiment, the same principles as discussed for Section 3.5 apply. If the measurements are similar to volumetric experiments, then Section 3.3 applies.

Table 2: (continued)

Accessible information and conditions of measurement

- Primary data: NMR signal and its dependence on the applied magnetic field gradient to access the spatial distribution and variation of molecules, with the option to additionally attain information about molecular properties, including their diffusivity.
- Sorbent needed: may vary from tens of milligrams to tens of grams.
- Time and spatial resolution are closely linked and, in addition, influenced by numerous factors including the type of molecules (nuclei) under consideration, their concentration, diffusivities, (nuclear magnetic) relaxation properties, and last but not least the performance of the measurement device. As a rule, NMR Imaging is mainly suited to diffusion studies with beds/pellets of sorbent crystallites/particles, with its application to single crystals/porous particles in so far only exceptional cases.

Strengths

- Spatially resolved observation of the filling/emptying of macroscopic nanoporous objects, including beds of pellets or crystals/particles, with the option of obtaining additional information about the guest molecules, including their (local) diffusivity.
- Observation of the filling/emptying of the individual pellets within a column.
- *In situ* observation and recording of the evolution of the distribution of the various components involved in a chemical reaction within a nanoporous catalyst.

Weaknesses and traps

- Errors due to mismatch in the applied pulse sequences.
- When used as on recording ACD (adsorption column dynamics, Section 3.5, now with focus on gas concentration inside the column rather than at the outlet), subject to the same weaknesses necessitating, for example, the application of a detailed model that includes heat and mass transfer in the column.

Tests of consistency

- Ensuring that the statements about the distribution and the properties of the molecules (e.g., their diffusivity) are left unchanged by a variation in the pulse sequences and/or the magnetic flux density.
- Measurement with guest molecules containing two different NMR-active nuclei (as typically ^1H and ^{13}C) have to yield coinciding results.
- Ensuring system is not under equilibrium control.

Pulsed Field Gradient (PFG) NMR (see Section 3.11)**Principle of measurement**

- The frequency of an NMR signal is determined by the externally applied magnetic flux density. Thus, by measurement with a suitable sequence of radiofrequency pulses in combination with two strongly inhomogeneous fields superimposed to the homogeneous one over two short time intervals (the field gradient pulses), the distribution of the diffusion path lengths of the molecules in the time interval between the two field gradient pulses contributing to the observed signal becomes accessible by considering the dependence of the NMR signal intensity on the intensity of the applied field gradients.

Accessible information and conditions of measurement

- “Microscopic” (“macroscopic”) measurement for main diffusion path lengths sufficiently short in comparison with (much larger than) the diameters of the crystals/particles under study.
- Primary data: NMR signal intensity recorded as a function of the field gradient intensity, yielding the Fourier transform of the “mean” propagator (i.e., the probability density of molecular displacement in field gradient direction, Eq. 56) and, hence, of also the molecular mean square displacements, giving rise to the self-diffusivity via the Einstein relation (Eq. 6).
- Sorbent needed: Tens of milligrams.
- Observation times: From milliseconds up to seconds, depending on the considered nuclei (generally protons) and the given relaxation times of transverse and longitudinal nuclear magnetization.
- Spatial resolution (observable displacements): From (under ideal conditions) fractions of up to hundreds of micrometers.

Strengths

- Measurement of mean diffusion path lengths providing direct access to molecular diffusion.
- Option of tracing internal resistances acting in addition to the transport resistance of the genuine pore space by varying the observation time and hence the mean diffusion path lengths.
- Selective diffusion measurement in multicomponent systems.
- Measurement during chemical reactions within porous catalysts and recording of the diffusivities of the various components and their variation.

Weaknesses and traps

- Recording of low diffusivities requires the application of particularly large magnetic field gradient pulses and large observation times which, notably with the nuclear magnetic relaxation properties typical of low diffusivities, are subject to particularly narrow limits. Diffusivities below about $10^{-13} \text{ m}^2\text{s}^{-1}$ are thus, as a rule, accessible in only exceptional cases.
- Especially in the case of large accumulation numbers, it may happen that only a minority (e.g., molecules in a few mesopores) contribute to the analyzed NMR signal, while (due to their “unfavorable” nuclear magnetic relaxation behavior) the majority of molecules, whose behavior one is actually interested in, remain unobserved.

Table 2: (continued)

Tests of consistency

- For measurement of both intracrystalline and long-range diffusion: Check that the resulting diffusivity is independent of the observation time.
- Under conditions where, during the PFG NMR experiments, the guest molecules are confined to the interior of the individual microporous crystals (e.g., by a total blockage of the intercrystalline space or by measurement at sufficiently low temperatures with the long-range diffusivity ($p_{\text{inter}}D_{\text{inter}}$) much smaller than the intracrystalline diffusivity (D_{intra})) comparison between the PFG NMR diffusivity attained in the limit of sufficiently large observation times and its estimate based on the crystal sizes serves as an independent check of validity for the attained diffusivities.
- Guest molecules containing different NMR-active nuclei (such as typically ^1H and ^{13}C) allow a validity check by demonstrating coincidence in the attained diffusivities by PFG NMR measurement with the different nuclei.
- By comparison with a standard, NMR provides the option of also determining absolute numbers of the nuclei contributing to the observed signal. Exploitation of this option avoids misinterpretation in assigning the recorded diffusivities to the “correct” molecules.

Quasi-Elastic Neutron Scattering (QENS, see Section 3.12)**Principle of measurement**

- Investigation of the scattering of a beam of neutrons after colliding with the nanoporous host–guest system under study, notably caused by their interaction with the nuclei contained therein. The distribution of energy and momentum exchange during the scattering process as appearing in a spreading in the speed and the direction of the scattered neutrons contains information about the microscopic dynamics of the scatterers. Scattering can be split into an incoherent (dominating with, notably, protons as the scattering nuclei) and a coherent (dominating, e.g., with nitrogen) part yielding, respectively, the self-diffusivity and (as a collective phenomenon) the transport diffusivity.

Accessible information and conditions of measurement

- Primary data: distribution in direction and energy of a flux of neutrons after colliding with the host–guest system, yielding the “differential cross section” as a measure of the fraction of neutrons scattered into a certain differential solid angle undergoing a certain energy exchange. Its (four-dimensional!) Fourier transform (into space and time) is the “Van Hove correlation function,” an equivalent of the mean propagator as attainable by PFG NMR (Eq. 55) but with notably smaller mean displacements, bearing information on possibly only internal molecular motion rather than on diffusion.
- Sorbent needed: Several grams.
- Observation times: From fractions of picoseconds to nanoseconds (depending on the measuring arrangement and the used technique).
- Spatial resolution (observable displacements): From fractions till tens of nanometers.

Strengths

- Measurement with diffusion path lengths over distances far below typical crystal/particle diameters allows (in particular in combination with PFG NMR) the detection, exploration, and quantitation of “intracrystalline” transport resistances operating in addition to the diffusional resistance of the genuine pore space.
- Depending on the chosen probe molecule (more precisely: Nucleus), both self- and transport diffusion become accessible. The latter option is based on the fact (regression theorem) that microscopic and macroscopic density variations are controlled by the same transport parameters.
- Selective diffusion measurement in multicomponent systems, using isotope substitution as an option to increase selectivity.
- Coincidence with molecular dynamic simulations in the covered space and time scales makes their combination particularly powerful.
- Given the accessibility of extremely small diffusion path lengths permits the measurement of intracrystalline/-particle diffusion without, essentially, any requirement concerning the crystal/particle sizes.
- Providing information at the transition between the elementary steps of diffusion to genuine intracrystalline diffusion makes QENS a particularly useful technique for exploring the mechanisms of molecular propagation under confinement and, thus, also an ideal partner in the discussion of the results of other measuring techniques (e.g., solid-state NMR – see Section 3.13).

Weaknesses and traps

- As a consequence of the need for sufficiently strong neutron sources and an adequate instrumentation, measurements can only be carried out at a few locations worldwide.
- Sufficiently large energy resolution of the scattered neutrons corresponding with diffusion times notably exceeding the duration of the elementary steps is often difficult to attain, setting a lower limit of about $10^{-13} \text{ m}^2\text{s}^{-1}$ to the accessible diffusivities.
- Observed scattering dependences are commonly analyzed by fitting to model approaches (e.g., by assuming diffusion by jumps) with, possibly, insufficient evidence for justification of their validity.

Tests of consistency

- Consistency checks by fitting to refined model approaches
- Overlap the dynamical ranges by using instruments with different energy resolution
- Careful selection and measurement of a background sample.

Table 2: (continued)

Solid-State NMR (see Section 3.13)**Principle of measurement**

- Amplitude and shape of the NMR signal are a function of the interaction of the considered nucleus (within the molecule under study) with its surroundings and of the variation in this interaction. There exist a number of options for exploiting the latter dependency for determining the mean life time of a molecule at a given position, providing valuable information about the elementary processes of molecular diffusion, possibly difficult to obtain by different techniques.
- Any statement on diffusion behavior must be based on model assumptions on the length of successive molecular jumps and their mutual interdependence.

Accessible information and conditions of measurement

- Measurement with focus on exclusively the elementary steps of diffusion, in particular of the mean life time between subsequent jumps.
- Primary data: NMR signal intensity and its variation in suitably chosen radio frequency pulse sequences, providing information about the mean time between subsequent jumps.
- Information about molecular diffusion (in particular: Self-diffusion) only in combination with assumptions concerning the jump length and their correlation, based on the known structure of the adsorbent and its interaction with the guest molecules.
- Sorbent needed: Tens of milligrams.
- Observation times (i.e., mean life time between subsequent steps): From microseconds till seconds.

Strengths

- Estimate of extremely small diffusivities down to about $10^{-19} \text{ m}^2\text{s}^{-1}$.
- Measurement with crystals/particles of any size.

Weaknesses and traps

- Estimation of diffusivities in only an indirect way, namely, based on assumptions on the mean jump length as resulting from the given host structure and the host-guest interaction.

Tests of consistency

- Coincidence with the diffusivities as resulting from other techniques, at least by extrapolation between the respective temperature intervals if there is no overlap in the ranges of measurement.

Single-Molecule Tracking (see Section 3.14)**Principle of measurement**

- Following the movement of individual fluorescent molecules within the nanoporous host material under study after laser light excitation in a series of snapshots by fluorescence microscopy, with subsequent “connecting of the points”.

Accessible information and conditions of measurement

- Measurement of individual molecular trajectories, that is, of molecular positions at subsequent instants of time as the primary data.
- Providing information about self-diffusion by considering the thus accessible mean square displacement as a function of time via Einstein relation, Eq. 6.
- Information about possible deviations from regular pore structure (detection, localization and characterization of traps, transport barriers, and fast diffusion paths) embedded within the regular pore structure.
- Spatial resolution: $\sim 2 \text{ nm}$ to $\sim 30 \text{ nm}$, with time resolution of $\sim 10 \text{ ms}$ to $\sim 30 \text{ ms}$.

Strengths

- Single molecule observation as a unique property, with impressively high spatial and time resolution (down to nanometers and tens of milliseconds).
- Observation (including localization) of chemical conversion.
- In situ observation with real-time monitoring.
- Monitoring in three dimensions with the option of three-dimensional profiling.

Weaknesses and traps

- Need for fluorescent probe molecules with properties (including their price) that are generally different from those of molecules used in commercial chemical plants and in studies using other measurement techniques.
- Analysis may be hampered by residual fluorescence of the host material (e.g., zeolites are notoriously known for their background fluorescence).
- Transparency of the host material as a prerequisite. The latter also means that the 3D measurement capabilities are limited to rather thin volumes.

Tests of consistency

- Assurance of conclusions by demonstrating the reproducibility of results obtained in a sufficiently large number of experiments under identical conditions.

Table 3: Symbols.

SI units (or SI derived units) are given in brackets. Dimensionless units are denoted by [–]. Parameters that are only needed in connection with the presentation of specific features of the respective measurement technique are not included.

Latin Letters

A	External surface of adsorbent host particle/crystal [m^2], column cross section [m^2]
b	Scattering length [m]
$\vec{B}_0$	Static magnetic flux density [T]
c	Guest concentration [mol m^{-3}], for macroscopic diffusion measurements more specific: Guest concentration in macropores (then, with the micropore concentrations denoted q)
c^*	Concentration of labeled guest molecules [mol m^{-3}]
c_F	Guest concentration on the feed side [mol m^{-3}]
C_p	Specific heat capacity of the gas [$\text{J}/(\text{kg K})$]
C_s	Specific heat capacity of the solid [$\text{J}/(\text{kg K})$]
D	Self-diffusivity (or tracer diffusivity or coefficient of self-diffusion), diffusivity in general (if not further specified) [$\text{m}^2 \text{s}^{-1}$]
D_0	Diffusivity in the limit of small concentrations (“limiting diffusivity”) [$\text{m}^2 \text{s}^{-1}$], here self- and transport diffusivities coincide
D_{eff}	Effective (or apparent) diffusivity in PFG NMR [$\text{m}^2 \text{s}^{-1}$]
D_c	Corrected (or Maxwell–Stefan) diffusivity [$\text{m}^2 \text{s}^{-1}$]
D_f	Fractal dimension [–]
D_{inter}	Self-diffusivity in the intercrystalline space [$\text{m}^2 \text{s}^{-1}$]
D_{iso}	Self-diffusivity of an isolated molecule [$\text{m}^2 \text{s}^{-1}$]
D_K	Knudsen diffusivity [$\text{m}^2 \text{s}^{-1}$]
$D_{\text{l.r.}}$	Long-range diffusivity in PFG NMR [$\text{m}^2 \text{s}^{-1}$]
D_m	Molecular diffusivity [$\text{m}^2 \text{s}^{-1}$]
D_P	Diffusivity in macropores [$\text{m}^2 \text{s}^{-1}$]
$D_{\text{s.f.}}$	Self-diffusivity in a single-file (“center of mass” diffusivity) [$\text{m}^2 \text{s}^{-1}$]
D_S	Surface diffusivity [$\text{m}^2 \text{s}^{-1}$]
D_{SP}	Contribution of surface diffusion to macropore diffusivity [$\text{m}^2 \text{s}^{-1}$]
D_T	Transport-diffusivity (or: Fickian diffusivity, coefficient of transport diffusion) [$\text{m}^2 \text{s}^{-1}$]
D_V	Viscous-flow related diffusivity [$\text{m}^2 \text{s}^{-1}$]
$D_{xx} \text{ (xy ...)}$	Elements of the diffusion tensor [$\text{m}^2 \text{s}^{-1}$]
D_{ij}	Element of the diffusion matrix correlating the flux of component i with the concentration gradient of component j [$\text{m}^2 \text{s}^{-1}$]
$\vec{\bar{D}}_{(T)}$	Tensor of (transport) diffusion [$\text{m}^2 \text{s}^{-1}$]
$D_{(T)i}$	Principle (transport) diffusivity = i th element of the diagonalized diffusion tensor [$\text{m}^2 \text{s}^{-1}$]
F	Carrier flow rate [m s^{-1}]
$F(t)$	Fractional uptake or release at time t [s^{-1}]
f	Friction coefficient [Pa m s]
g	Magnetic field gradient [T m^{-1}]
G	Overall transfer function relating response to perturbation in FR [–]
$G_{S,D}(\vec{r}, t)$	Probability density that, after time t , the same (S) or a different (D) nucleus will be at a position shifted by the vector $\vec{r}$ (Van Hove correlation functions) [m^{-1}]
H	Height equivalent to a theoretical plate (HETP)
$\hbar$	Reduced planck constant [J s]
j	molar flux [$\text{mol s}^{-1} \text{m}^{-2}$]
j^*	flux of labeled molecules [$\text{mol s}^{-1} \text{m}^{-2}$]
k	Wave vector of a neutron beam [m^{-1}]
k_B	Boltzmann constant [J K^{-1}]
k_f	External film resistance in the fluid phase [ms^{-1}]
K	Henry’s law constant (limiting slope of the adsorption isotherm $q(c)$ as commonly considered in macroscopic diffusion measurements) [–]
l	Half plate thickness [m]
L	(Single-file) length [m], ratio between the diffusion time (R^2/D) and the <i>washout</i> time of the adsorbed phase [–]

Table 3: (continued)

L_c	Length of the packed section of a column [m]
m	(Neutron) mass [kg]
M	Molecular mass [kg mol ⁻¹]
$M_0(\vec{r})$	Net equilibrium nuclear spin magnetization in a voxel at position $\vec{r}$ in MRI [A m ⁻¹]
M_1	First statistical moment of molecular uptake [s]
$M_{1, \text{dif}}$	First statistical moment of molecular uptake under diffusion limitation [s]
$M_{1, \text{sur}}$	First statistical moment of molecular uptake under limitation by surface barriers [s]
N	Total number of scatterers [–]
p	Pressure [Pa], momentum [kg m s ⁻¹]
p_{inter}	Relative number of molecules in the intercrystalline space [mol mol ⁻¹]
$P(x, t)$	Probability (density) of molecular displacement over x in x -direction during t (=propagator) [m ⁻¹]
q	Micropore guest concentration [mol m ⁻³], intensity of the field gradient pulses
q_E	Micropore guest concentration in equilibrium with the macropore concentration [mol m ⁻³]
Q_0	Quadrupole coupling constant [Hz]
r	Pore radius or distance [m]
R	Radius of adsorbent host particle/crystal [m]
R_g	Universal gas constant [J mol ⁻¹ K ⁻¹]
S	Signal intensity in MRI (of a voxel at position $\vec{r}$) and PFG NMR [–]
$S_{\text{inc. (coh)}}$	Incoherent (coherent) scattering function [–]
t	Time [s]
t_{dif}	Square of the characteristic dimension of the adsorbent particle divided by the diffusivity; diffusion time [s]
T	Temperature [K]
T_2^*	Effective spin-spin relaxation time in MRI [s]
u	Molecular mean velocity [m s ⁻¹]
v	(Neutron) velocity [m s ⁻¹]
V_S	Volume of adsorbent host particle/crystal [m ³]
$x_{(i)}$	Cartesian coordinate(s), $i = 1, 2, 3$ [m]
X	Spatial coordinate through the pellet [m]
Greek letters	
α	Permeability of a transport barrier in the particle/crystal interior or on its surface [m s ⁻¹], lumped heat transfer coefficient in FR [J/(K s)]
γ	Ratio of the accumulation in the fluid over the adsorbed phase [–], gyromagnetic ratio [T ⁻¹ s ⁻¹]
δ	Duration of the magnetic field gradient pulses in PFG NMR [s], thickness of a membrane [m], Dirac's delta function
ε_p	Void fraction of macropores [–]
η	Viscosity [kg m ⁻¹ s ⁻¹]
θ	Pore filling factor [–]; scattering angle
λ	Separation between adjacent adsorption sites [m], heat of adsorption (taken to be negative) [kJ mol ⁻¹], wave length [m]
μ	Chemical potential [J mol ⁻¹], first moment in an adsorption column [s]
ν_L	Larmor frequency [Hz]
$\rho(\vec{r})$	Nuclear spin density at position $\vec{r}$ [m ⁻³]
σ	Scattering cross section [m ²]
σ^2	Second moment in an adsorption column [s ²]
τ_c	Correlation time of molecular reorientation [s]
τ	Molecular mean life time [s]; tortuosity [–]
φ	Precessional phase in NMR [rad]
ψ	PFG NMR signal attenuation [–]
ψ_s	Wave function in QENS [m ^{-3/2}]
ω	Angular frequency [rad s ⁻¹]
Ω	Solid angle [sr]

Table 4: Abbreviations.

ADC	apparent diffusion coefficient (in MRI)
AlPO ₄ -5	aluminum phosphate molecular sieve number 5
BS	Backscattering
COF	covalent organic framework
CSFR	concentration-swing frequency response
CNTs	carbon nanotubes
CT	Computed Tomography
DCB	dynamic column breakthrough curve
DGM	dusty gas model
EMA	effective medium theory of approximation
FAU	synthetic aluminosilicate zeolite named after the mineral Faujasite
FCC	Fluid Catalytic Cracking
FR	Frequency Response
HETP	height equivalent to a theoretical plate
HU	Hounsfield unit
IFM	interference microscopy
IRM	infrared microscopy
IUPAC	International Union of Pure and Applied Chemistry
LDF	Linear driving force
MAS	magic-angle spinning
MD	molecular dynamics
MFC	mass flow controller
MFI	Mobil Five-ring, a zeolite structure. The Al-containing MFI is called ZSM-5, the Al-free one silicalite-1
MFV	mass flow meter
MOF	metal-organic framework
MRI	Nuclear Magnetic Resonance Imaging
MS	mass spectrometer
NFR	nonlinear frequency response
NMR	Nuclear Magnetic Resonance
NSE	neutron spin echo
PDI	2,6-dimethylphenyl)-perylene-3,4,9,10-tetracarboxylic diimide
PFG NMR	Pulsed Field Gradient NMR
PGSE NMR	Pulsed Gradient Spin-Echo NMR
PL	partial loading experiment
PSF	point spreading function
PSFR	pressure-swing frequency response
PTFE	polytetrafluoroethylene
PT	pressure transducer
QENS	Quasi-Elastic Neutron Scattering
RF	radio frequency
SFA	smooth field approximation
SMF	single-molecule fluorescence (in microscopy)
SNR	signal-to-noise ratio
TDI	terrylenediimide
TOF	Time-of-Flight
TST	transition state theory
VGO	vacuum gas Oil
VSFR	volume-swing frequency response
ZIF	zeolitic imidazolate framework, an MOF sub-family
ZLC	Zero length column
ZSM-5	Zeolite Socony Mobil-5 with MFI structure
8 MR	eight-membered ring (in zeolites).

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