

The Beauty of the Different Views on Diffusion

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Diffusion is the irregular motion of the elementary constituents of matter such as atoms and molecules, sustained by their thermal energy. It is among the most fundamental, ubiquitous phenomena in nature ⁽¹⁻⁴⁾, ensuring the functionality of living cells ⁽⁵⁾ just as the performance of numerous technologies towards value-added products ⁽⁶⁾.

Depending on the topics of investigation, diffusion phenomena may be traced over length scales ranging from nano- to kilometers and femtoseconds to ages. Irrespective of these huge differences, the observed phenomena are often found to obey generally applicable, unifying rules. This is in striking contrast to the great challenges one is often confronted with in diffusion measurements with a particular system and which, generally, turn out to be very specific.

Among the countless systems investigated with respect to their diffusion properties, nanoporous materials are distinguished in a threefold manner, namely (i) by their technological relevance for matter upgrading by, e.g., heterogeneous catalysis ⁽⁷⁾ and selective adsorption ⁽⁸⁾ and the role of transport phenomena in these application, (ii) by their relevance for fundamental science as host materials for the investigation of mesoscopic systems and particle ensembles under confinement and (iii) by their exceptional position as a model system which allows to visualize the multitude of diffusion phenomena in immediate visual perception. It is this latter aspect which is in the focus of this talk.

A Discrepancy of Five Orders of Magnitude

The utmost information accessible about diffusion phenomena in a given system is contained in the so-called propagator $P(\mathbf{r}_0, \mathbf{r}_0 + \mathbf{r}; t_0, t_0 + t)$. It denotes the probability (density) that a particle, which is found at position \mathbf{r}_0 at time t_0 , will have moved to position $\mathbf{r}_0 + \mathbf{r}$ at time $t_0 + t$. With the introduction of the pulsed field gradient technique of nuclear magnetic resonance (PFG NMR, also referred to as the pulsed gradient spin echo (PGSE) technique or NMR diffusometry ⁽⁹⁻¹¹⁾), for the first time, the mean value $\langle P(\mathbf{r}_0, \mathbf{r}_0 + \mathbf{r}; t_0, t_0 + t) \rangle_{\mathbf{r}_0} \equiv P(\mathbf{r}, t; t_0)$ of this quantity has become experimentally accessible ⁽¹²⁾.

As a typical example of the evidence provided by this type of experiment, Figure 1 displays propagator representations for ethane as guest molecules in a crystalline microporous material (zeolite of type NaCaA) with particle sizes of about 1 and 16 μm . The measurements are performed in closed sample tubes after attainment of equilibrium so that the mean propagator does not vary anymore with the instant t_0 of the measurement. It may, hence, be noted $P(\mathbf{r}, t)$ where, in Figure 1, the "observation" time, following the usual nomenclature of PFG NMR, is expressed by Δ rather than t . For sufficiently large crystals and sufficiently small diffusivities and observation times t (top left), molecular propagation inside the crystals is essentially independent of disturbing effects by the crystal boundary and the intercrystalline space. Under such conditions, one obtains the intracrystalline self-diffusivity D via the Einstein relation $\langle z^2(t) \rangle = 2Dt$ from the mean squared width of the distribution, i.e. the mean square lengths of the molecular trajectories during time t .

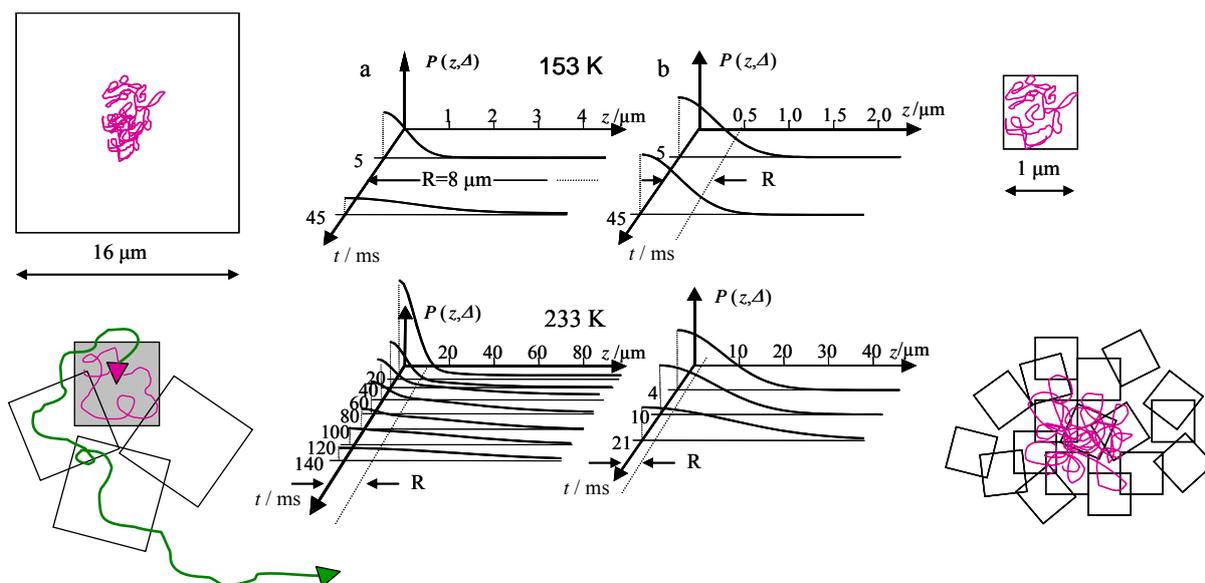


Figure 1: Experimental evidence provided by PFG NMR: The mean propagator of ethane as guest molecules in beds of nanoporous crystallites (zeolite of type NaCaA) of different size and cartoons of typical diffusion paths under the considered situations ^(12,13).

Under spatial confinement (top right) the mean square displacement is a measure of the size of the confining region. This type of “microscopy” is referred to as “dynamic imaging”^(9,14). Bottom right illustrates the situation when PFG NMR is studying the diffusivity through a crystal bed. The resulting (“long-range”) diffusivity $D_{lr} = p_{inter}D_{inter}$ is the product of the relative amount of molecules in the intercrystalline space and their diffusivity and may, as a most notable feature, significantly exceed the diffusivity in the fluid phase ^(15,16). Bottom left, finally, illustrates a situation where only a fraction of the molecules are able to leave the crystals. This fraction is directly provided by the integral under the corresponding constituents of the propagator (the broad base line). It may thus be determined as a function of the observation time. The provided information is that of a conventional tracer exchange experiment, with the important difference that the exchange times are in the range of milliseconds and that any disturbing influence by bed effects may be excluded ^(13,17).

As the most spectacular outcome of the application of PFG NMR to nanoporous materials, notably to zeolites as their most important representative ^(18,19), the thus determined values of intracrystalline diffusivities were found to exceed the previously determined ones in several cases by as much as five orders of magnitude ⁽²⁰⁾! One had to conclude, therefore, that the processes recorded in all these former studies were limited by phenomena different from the diffusional resistance in the genuine pore network, including transport resistances at the external surface of the crystallites and internal resistances by stacking faults ⁽²¹⁾. Remaining essentially unobservable by conventional structural analysis, it was thus not before the introduction of these novel techniques of diffusion measurements ⁽¹³⁾ that the deviations in crystal structure giving rise to these additional obstacles could be detected!

The revision of the view on intracrystalline diffusion initiated by these NMR experiments gave rise to a real flood of novel techniques operating under both equilibrium and non-equilibrium conditions. Figure 2 provides an impression of this dramatic development.

Year of First Application of Diffusion Measuring Techniques

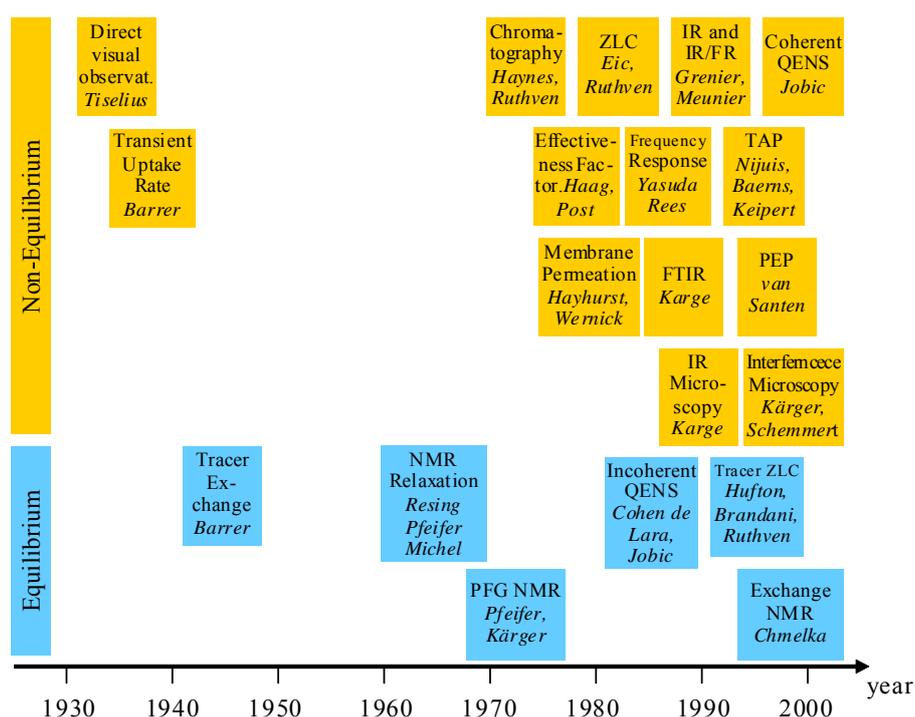


Figure 2: Temporal sequence of the introduction of the different methods of diffusion measurement in porous materials (zeolites) by ensemble techniques^(13,22)

Combining the Evidence of NMR Diffusometry and Magnetic Resonance Tomography (MRT)

The novel view on the rate of molecular diffusion in nanoporous materials as evidenced by PFG NMR necessitated a revision of the conventional assumption that, in most cases, overall adsorption is limited by uptake on the individual crystallites. It was in exactly that time when Paul Lauterbur⁽²³⁾ demonstrated the potentials of nuclear magnetic resonance for imaging. Based on ingenious developments in NMR processing by Richard Ernst⁽²⁴⁾ and Peter Mansfield⁽²⁵⁾, today this method has become one of the most powerful imaging techniques in medical diagnosis, known under the name magnetic resonance tomography (MRT), with a continuously growing spectrum of further applications^(26,27). Figure 3 illustrates that, already at a very early stage in its development and long before it has become a routine technique, MRT was exploited for visualizing how the interrelation between intracrystalline and long-range diffusion as revealed by PFG NMR did as well appear in the concentration patterns during molecular uptake by beds of crystallites.

The patterns of concentration evolution are controlled by the relation between the time constants of bed uptake ($\tau_{\text{bed}} \sim L^2/D_{\text{long-range}}$, with L denoting the bed extension) and of uptake by the individual crystallites ($\tau_{\text{intra}} \sim d^2/D_{\text{intra}}$, with d denoting the crystal size). Thus, under the conditions leading to the patterns of Figures 3 b and c (with the notably smaller crystallite radii), the ratio $\tau_{\text{intra}}/\tau_{\text{bed}}$ is expected to assume much smaller values than under the conditions considered in Figure 3a. In complete agreement with this consideration, in Figure 3 b the NaCaA crystals in the first layer are seen to be saturated very rapidly by the guest molecules. Only in a second, much slower process (Figure 3 c) do the molecules, from this first layer, distribute through the whole bed of crystals. In the bed of large crystals (Figure 3 a), however, the guest molecules are found to be distributed essentially instantaneously over the whole bed, with molecular uptake occurring essentially simultaneously in all crystals.

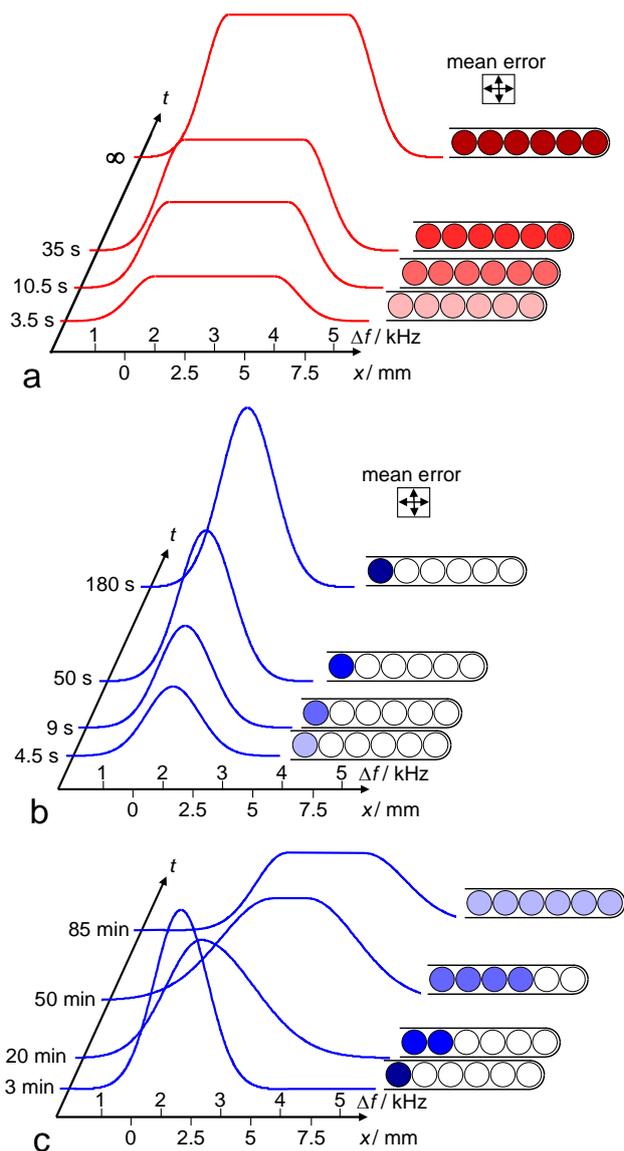


Figure 3: Evolution of the distribution of n-butane in a bed of crystals of zeolite NaCaA with crystal diameters of about 40 μm (a) and 4 μm (b,c) in an NMR sample tube in axial (x -) direction as appearing in the NMR spectrum under the conditions of MRI (left) and visualized by cartoon plots (right). After activation, the sample has been brought into contact with a finite volume of gaseous n-butane (at $x = 0$, the opening of the sample tube). Limitations in spatial resolution flatten ascending and descending parts in the profiles. Redrawn from ⁽²⁸⁾

Nuclear magnetic resonance continues to provide us with impressive novel insights, even today, more than half a century after its detection by Bloch ⁽²⁹⁾ and Purcell ⁽³⁰⁾. The ability to trace displacements over tens of nanometers ⁽³¹⁾ and to record images with resolutions in the range of micrometers ⁽²⁷⁾ and diffusion measurements in the limit of small concentrations filling the gap between ensemble and single-molecule measurements ⁽³²⁾ are achievements characterizing the most recent progress in the field. The combination of gravimetric uptake and PFG NMR diffusion measurement for elucidating the century-old mystery of the equilibration rates during adsorption hysteresis ⁽³³⁾ and of magic angle spinning (MAS) NMR, originally developed for obtaining highly resolved NMR spectra with solids ⁽³⁴⁾, with PFG NMR for facilitating selective diffusion measurements are further examples of most recent progress in the field of NMR diffusometry ⁽³⁵⁾.

Irrespective of this remarkable progress, the possibilities of the various NMR techniques do not yet suffice to record transient concentration profiles in the interior of the individual crystallites of these nanoporous materials. This limitation in diffusion research has now been overcome by the application of micro-imaging techniques based on interference and IR microscopy ^(13,36), which are in the focus of the second half of the presentation.

Unprecedented Wealth of Information on Guest Dynamics in Nanoporous Host Systems

While PFG NMR yields the probability distribution of molecular propagation as an average taken over the whole sample volume, micro-imaging techniques based on interference and IR microscopy are able to record the development of the local concentration in a particular crystallite. Figure 4 illustrates the wealth of information which becomes accessible by this type of experiments.

Figure 4c shows the transient concentration profiles in 2-d plots measured 50 and 270 seconds after the onset of methanol uptake by a crystal of manganese formate (Figs. 4 a and b)^(37,38). Manganese formate is a representative of the metal organic frameworks (MOFs) which have recently emerged as a novel class of nanoporous materials⁽³⁹⁾. Concentration profiles along the longitudinal extension (which coincides with the direction of the pore chains within the crystal – see Figure 4b) for many more time steps are shown in Figure 4d. The profiles illustrate the particular beauty of such experiments which, by exploiting the potentials of the profiling techniques in solid-state physics and the benefit of the high guest diffusivities, are able to provide experimental data of unprecedented wealth. The key parameters of mass transfer resulting from such experiments, namely the intracrystalline diffusivities and the permeability through the crystal surface, are shown in Figure 4e. Their notably different dependence on the guest concentration may be easily referred to the fact that intracrystalline diffusion and permeation through the crystal surface must, in general, be understood as two totally different phenomena of mass transfer. The possibility to measure these two key parameters of mass transfer in dependence on the nature of the considered host and guest systems, on their loadings and on the temperature opened a new field in the diffusion research with molecules under confinement.

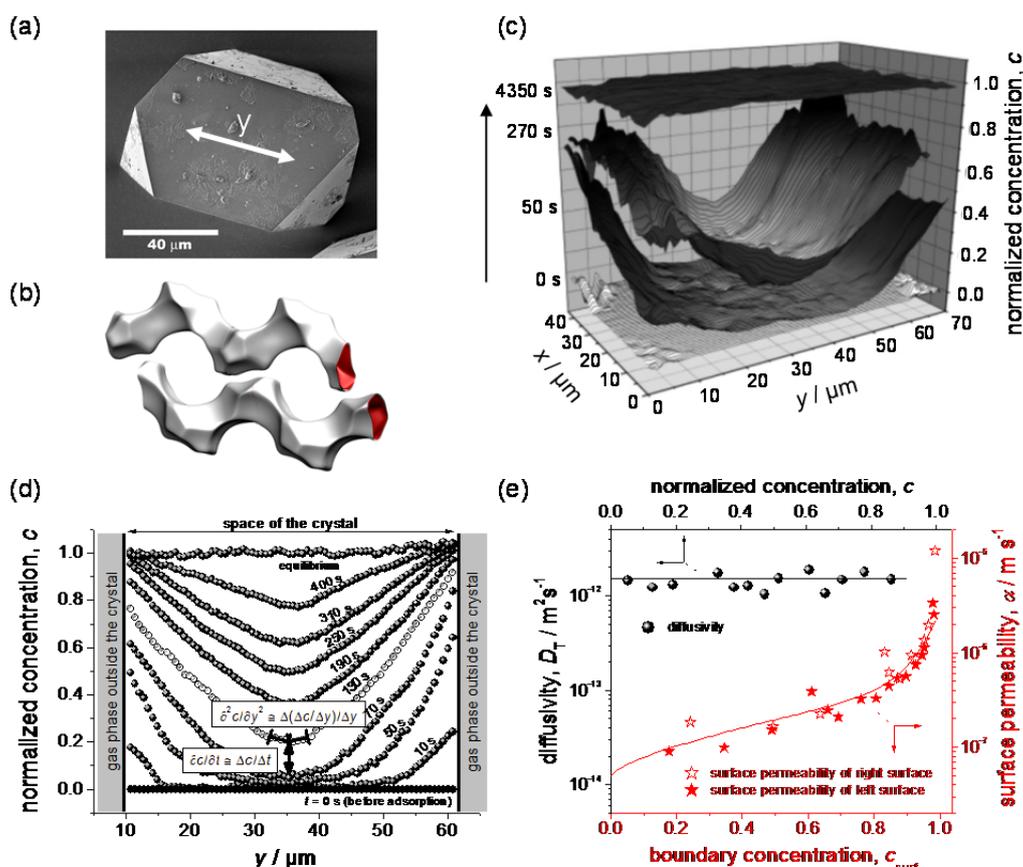


Figure 4: Methanol uptake by MOF manganese formate by a pressure step from 0 to 10 mbar at 298 K as studied by IFM, with a typical crystal under study (a) and schematics of the pore structure (b). From the two-dimensional concentration plots (c), best profiles could be determined at $x = 41 \mu\text{m}$ (d), leading to the transport diffusivities and surface permeabilities as shown in (e).⁽³⁸⁾

Constant Diffusivity-Permeability Ratios, Fluxes Accelerated by Counter Fluxes and Further Surprises

With the new tool of micro-imaging in our hands, a large spectrum of phenomena became accessible by direct experimental observation, with some of them so far even unknown to exist. These new options do in particular concern the possibility to determine the passage rate of the guest molecules through the interface between the nanoporous solid and the surrounding atmosphere. The existence of transport resistances in these interfaces, the so-called “surface barriers”, was postulated long time ago, namely as a possible explanation of the discrepancy between the diffusion data of the “novel” PFG NMR technique and conventional macroscopic measurements⁽²⁰⁾. Only now, however, it became possible to determine these resistances with a sufficiently high accuracy, allowing the exploration of their origin.

Most remarkably, surface resistances were found to represent a quite common phenomenon. So far, only in rather exceptional cases⁽⁴⁰⁾ molecular exchange between the crystals and the surrounding atmosphere was found to be exclusively determined by intracrystalline diffusion. In general, as illustrated by Figure 4e, intracrystalline diffusion and surface permeation were found to follow different dependences. It was therefore taken as a great surprise when in the MOF-type nanoporous materials Zn(tbip)⁽⁴¹⁾ the intracrystalline diffusivities and surface permeabilities were found to follow identical trends⁽⁴²⁾. This finding is most impressively quantified by considering the ratio between these two quantities⁽⁴³⁾ which, for a given crystallite, is found to remain unaffected by varying (i) the nature of the molecules, (ii) their concentration and (iii) the temperature, even each of these two quantities varies over orders of magnitude!

With these findings, for the first time a well-defined description of the mechanisms leading to the surface resistance of a nanoporous solid has become possible: In contrast to the conventional view that these resistances are brought about by a thin layer of dramatically reduced diffusivity or solubility of the guest molecules, one has to require that there is an essentially unrestricted passage through a small number of “windows” in an otherwise impermeable surface. This conclusion could be confirmed by both analytical arguments in the effective-medium approach^(44,45) and by dynamic Monte Carlo simulations using the model shown in Figure 5⁽⁴⁶⁾.

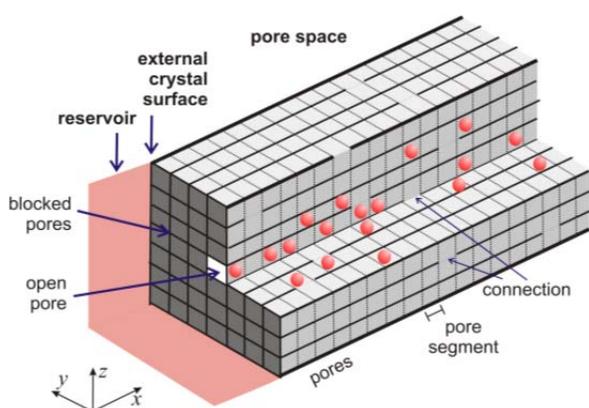


Figure 5: Structure model for confirming proportionality between intracrystalline diffusion and surface permeation⁽⁴⁶⁾ as reported in refs.^(42,43) for the nanoporous material MOF Zn(tbip). The host system consists of 1d channels, where adjacent channels are connected at defect sites occurring with a probability p_y and p_z , respectively. Only a small fraction p_{open} of the channel mouths are open, i.e. molecules may enter into these channels directly from the surroundings.

In parallel to the quantification of transport resistances on the surface of nanoporous materials, micro-imaging did as well allow to determine the probability that, on colliding with the external surface of the particle, a molecule out of the surrounding atmosphere will be able to overcome the surface resistance and propagate further into the interior. The resulting probability is the equivalent to the sticking coefficients well-known from chemisorption and heterogeneous catalysis⁽⁴⁷⁾. Like the sticking coefficients in heterogeneous catalysis, the “sticking probabilities” of guest molecules by nanoporous materials are found to notably vary with the host-guest system under consideration. So far determined values^(13,48) range from the order of 10^{-5} for methanol in ferrierite-type crystallites⁽⁴⁹⁾ up to 0.01 for isobutane in silicalite-1⁽⁵⁰⁾.

Micro-imaging by IR microscopy offers the unprecedented option to measure guest diffusion in nanoporous materials under both equilibrium and non-equilibrium conditions within one and the same experimental setup under directly comparable conditions. Figure 6 shows a particularly impressive result of these new possibilities⁽⁵¹⁾. The data displayed in this representation provide the experimental confirmation of three predictions of diffusion theory which, due to experimental difficulties and limitations inherent to all experimental techniques so far employed, never before have been possible in a comparably convincing way, namely

(i) the coincidence of the diffusivities measured in the limit of vanishing concentrations under equilibrium (D_{self}) and non-equilibrium (D_T) conditions (which, depending on the respective community, are referred to as the self- or tracer diffusivity and as the transport, collective or chemical diffusivity, respectively^(1,11,52)),

(ii) the coincidence of the self-diffusivity with the so-called corrected transport diffusivity (D_{T0}), given the fact that the rate of guest propagation is controlled by the jump rate through the “windows” between adjacent (nano)pores rather than by the rate of redistribution within the individual (nano)pores (it holds $D_{T0} = D_T \partial \ln c / \partial \ln p$, with $c(p)$ given by the adsorption isotherms as exemplified in Figure 6d) and

(iii) self-diffusivities (as a measure of the rate of molecular fluxes opposed by identical fluxes of labelled (tracer) molecules) exceeding the transport diffusivities (referring to fluxes without these counter fluxes) if a strong guest-guest interaction leads to S-shaped isotherms as, among the systems considered in this study, observed for methanol in MOFs of type ZIF-8 over the whole concentration range and for ethanol up to relative pore fillings of about $\Theta = 0.5$.

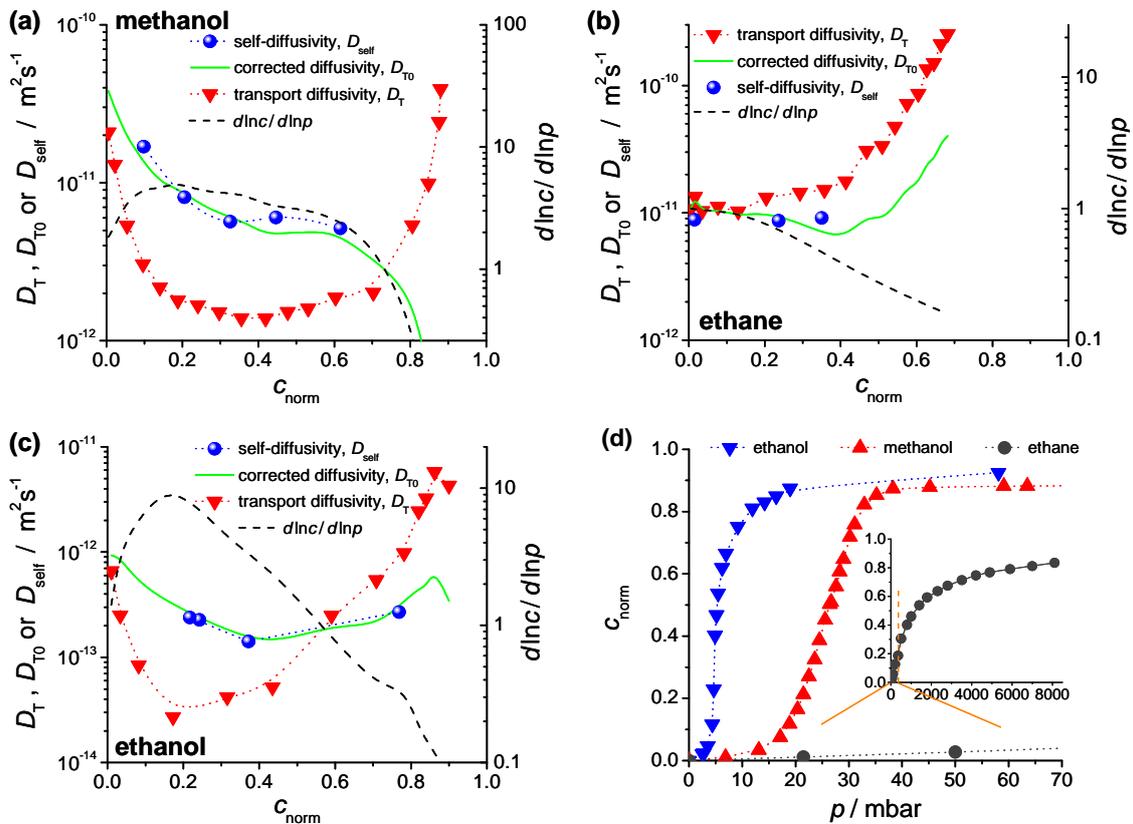


Figure 6: Methanol, ethane, and ethanol in ZIF-8 at 298 K. Loading dependence of transport (D_T), corrected (D_{T0}), and self-diffusivity (D_{self}) of (a) methanol (MeOH), (b) ethane, and (c) ethanol (EtOH). The quantity $\partial \ln c / \partial \ln p$ (the inverse “thermodynamic factor”) obtained from (d) is also shown. (d) Adsorption isotherms: the isotherms of methanol and ethanol exhibit a pronounced “S shape” whereas the isotherm of ethane shows the usual behavior of dominating host-guest interaction. For all molecules the loading at saturated vapor pressure corresponds to complete pore filling, i.e. $\Theta = 1$ ⁽⁵¹⁾.

Conclusion and Acknowledgement

Diffusion is a truly interdisciplinary field. Being intimately correlated by the common features of random-walk phenomena, mutual exchange between the different communities bears a wealth of possibilities for strengthening research in each particular realm. The Diffusion-Fundamentals Online-Journal www.diffusion-online.org, in combination with an accompanying conference series of tutorial character ^(4,53,54) is dedicated to this unifying aspect. I am deeply obliged to the organizers of the DSL CONFERENCE 2011, in particular to Andreas Öchsner and Graeme Murch, for inviting me to this event and for giving me the chance to provide examples which illustrate these unifying aspects of diffusion theory, experiment and application in front of a wide audience comprising researchers, scientists and engineers from industry, research laboratories and academia.

With deep gratitude I refer to the fortunate conditions under which I could start my scientific career in the NMR group founded and directed over many years by Harry Pfeifer ⁽⁵⁵⁾ at Leipzig University. With Wilfried Heink, Günter Seiffert and Petrik Galvosas, I had dear colleagues and excellent experimentalists by my side who made it possible that there was scarcely another place in the world where PFG NMR diffusion measurements could be performed with higher accuracy and sensitivity. I am obliged to Dieter Freude for his recommendation many years ago to make diffusion the topic of my thesis and for accompanying me on quite a number of random walks in this fascinating field of research. With particular pleasure I acknowledge the collaboration with my young colleagues Rustem Valiullin and Christian Chmelik and their students which, even after retirement, provides me with an ample field for continued scientific activities.

My acknowledgement would, clearly, be incomplete without referring to manifold co-operations with colleagues in other groups in our University, all over Germany and abroad. Many of them are among the authors of the citations given at the end of this presentation. It is with particular thanks and obligation when I refer, in this context, to Reinhold Haberlandt (Leipzig) ⁽⁵⁶⁾, Paul Heitjans (Hannover) ⁽¹⁾, Douglas Ruthven (Orono, USA) ⁽⁵⁷⁾ and Doros Theodorou (Athens) ⁽¹⁹⁾, and our efforts to contribute with joint editions to the exchange of ideas within our large community. Last, but not least, I thank my wife Birge for all her patience, understanding and support.

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