In Memory of Prof. Dr.-Ing. Jens Weitkamp

In bidding farewell to Prof. Dr.-Ing. Jens Weitkamp, we remember his many activities and his beneficial influence on the development of science, notably in the various fields of chemical technology and engineering. These activities include his engagement in support of the development of techniques dedicated to improvement of our understanding of the complex phenomenon of mass transfer in nanoporous materials, as both an ingenious scientist and a brilliant organizer and gifted leader of scientific alliances. The present contribution provides a brief introduction to the many facets of research in this field, with particular recognition of the most recent developments and Prof. Weitkamp’s contributions.

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1 Introduction

Several detailed treatises are available dealing with the investigation and application of nanoporous solids, with special reference to the evaluation of their surface area and pore width distribution based on a wealth of experimental studies and theoretical investigations extending over close to a century [1–6]. In 1985 an IUPAC manual was published on reporting physisorption data for gas/solid systems [7], with a first update by Thommes et al. [8] in 2015. An informative overview may be found in [9].

Like adsorption, diffusion is also among the key phenomena characterizing the behavior of molecules in interaction with solid surfaces. This relevance equally concerns their significance for fundamental research and the practical application of these materials, notably including nanoporous solids. Such materials are distinguished by their large specific surface area and their pore width in the range of molecular size that allows intimate contact with the guest molecules as a prerequisite for their upscaling by selective catalytic conversion and/or separation.

It is this interaction which, on the other hand, may dramatically impede the speed of molecular propagation, ending up in a significant reduction in the molecular diffusivity and, hence, in the rate of molecular exchange between the interior of the nanoporous particles and their surroundings. This rate determines the maximum possible speed at which value-added substances can be produced. Knowledge of this rate and, hence, of the various processes of internal mass transfer is, therefore, of crucial relevance for the proper understanding of the phenomena within the nanoporous materials and thus for a knowledge-based enhancement of performance in their technological application.

Diffusion of guest molecules in nanoporous materials and their adsorption properties are thus seen to be of comparable relevance for the practical application of these materials. This equivalence, most remarkably, is in no way reflected by the attention that is generally given to these phenomena. For example, within the Web of Science Core Collection in January 2021, in Microporous and Mesoporous Materials, the total number of papers so far published under the topic “Adsorption” is found to be 4804, while under the topic “Diffusion” it is only 901. For Adsorption – Journal of the International Adsorption Society the corresponding numbers are 1647 and 313. Within the key journals dealing with nanoporous solids and adsorption phenomena, molecular adsorption is thus seen to receive five times more attention than diffusion. This imbalance is, largely, related to the particular challenges that one is confronted with when investigating guest diffusion in nanoporous materials. Conditions of measure-

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The success of these old PFG NMR diffusion measurements at Leipzig University in the 1970s and 1980s were, on the one hand side, related to the local tradition in the application of nuclear magnetic resonance. It may be traced back to Felix Bloch, Werner Heisenberg’s first PhD student in Leipzig. Together with Edward Purcell, he was honored with the 1952 Nobel Prize in Physics for his work on the detection of NMR, which he had carried out at Stanford after his escape from Nazi Germany. Notably under the direction of Artur Lösche [41] and Harry Pfeifer [33, 42], starting with the 1950s Leipzig became an internationally renowned center of NMR, which Richard Ernst, Nobel Prize Laureate 1991, characterized as the East Pole of nuclear magnetism [43].

Leipzig’s position east of the Iron Curtain was, in fact, the second essential prerequisite for the new view on diffusion
in zeolites emerging with the application of PFG NMR. Differing from Michel Boudart and colleagues, who applied this novel NMR technique for the first time to diffusion measurement in zeolites [44], researchers in Leipzig benefited from their direct contact with Sergey Petrovich Zhdanov in Leningrad, Soviet Union, and their access to the largest zeolite crystals that had, in those days, been synthesized [45, 46]. Thus, for the very first time, PFG NMR diffusion measurements could be performed with displacements much smaller than the crystal diameters, which is a prerequisite for the unambiguous measurement of intracrystalline, i.e., of genuine micro pore, diffusion [32, 47].

Being based on a measuring principle totally different from diffusion studies by uptake and release and yielding, in numerous cases, diffusion data notably deviating from what so far has been known and generally accepted [34], the advent of PFG NMR had been met, by parts of the community, with some skepticism [35, 36]. In these first years of application to diffusion measurement in zeolites, the development of PFG NMR benefited significantly from collaboration within the Eastern countries. It was notably enabled by their Academies of Sciences, within a cooperation network with colleagues in Berlin [48], Prague [49], Moscow [50] and Leningrad [51].

This network facilitated the formation of contacts with their colleagues on the other side of the Iron Curtain [39, 52–54]. The textbook “Diffusion in Zeolites and Other Microporous Solids” [55] emerging from these contacts (with so far more than 2700 citations according to Google Scholar) illustrates their fertility. For their research work, in 1993 the authors of this book (Jörg Kärger and Douglas M. Ruthven) were honored with the Max Planck Research Award of the Alexander-von-Humboldt Foundation and the Max Planck Society, followed by D. M. Ruthven’s recognition with the Humboldt Research Award in 2002. Wide-ranging motivation and support by the Alexander-von-Humboldt Foundation ensured their continued cooperation up to these days, including the edition of a follow up of their diffusion textbook [26] with the addition of Doros Theodorou as a co-author.

The fall of the Iron Curtain in 1989 and Germany’s reunification also offered novel, unprecedented perspectives of funding and cooperation in diffusion research. In Leipzig, generous support by the German Research Foundation (DFG) allowed the development of interference microscopy (IFM) as a novel technique of diffusion measurement, based on the observation of the evolution of intracrystalline concentration profiles [56]. The potential of this new technique was further enhanced by the application of IR microscopy (IRM) for the same purpose [57, 58], giving rise to an experimental approach referred to as microimaging [59] as an experimental technique that allowed, for the very first time, microscopic diffusion measurement under transient conditions [60].

All these developments largely benefited from support by the German Zeolite Association, which was formed under the auspices of the German Society for Chemical Engineering and Biotechnology (DEchema). It is for this very process that Jens Weitkamp deserves recognition for all his efforts over many years as DEChema’s vice president. His activities extended far beyond strategic-organizational matters and did, in particular, concern core issues of science. A main focus of these activities was on the combined effect of diffusion and catalytic conversion.

Highlights among these studies were the investigation of the influence of diffusion on chemical reactions in microporous single-file systems [61] and in fluid catalytic cracking (FCC) catalysts [62, 63]. These latter studies have been performed within the GROWTH programme of the European Community (2001–2004) in a collaborative network consisting of nine partners from five countries. Jens Weitkamp saw his particular role in the synthesis of nanoporous materials of exactly the nature required for the particular diffusion measurement technique, including their subsequent modification. Examples include studies with zeolite X where a controlled variation of the cation content was demonstrated to lead, as a function of the nature and concentration of the exchangeable cations, to guest diffusivities both increasing and decreasing with guest concentration [64]. Particularly impressive results were obtained with the synthesis of ultra-large crystals of zeolite ferrierite [65–67]. Depending on the mode of synthesis and subsequent sample treatment, molecular uptake and release could be shown to occur in either one [68] or two dimensions [60].

With the many facets that proved to be critical for mass transfer in nanoporous materials, the study of diffusion became more and more a topic of international cooperation. Within the German Research Foundation, with input from DEChema and, notably, from Jens Weitkamp, this tendency was taken account of with the formation of an International Research Training Group jointly sponsored by the DFG and its partner organization (NOW) in the Netherlands, connecting Leipzig with researchers in Delft, Eindhoven, Amsterdam and Utrecht [65, 69–74] and with an International Research Team on diffusion in zeolites jointly sponsored by CNRS (France), EPSRC (UK), NSF (USA) and DFG (Germany) [69, 75, 76].

Internationalization of diffusion research was accompanied by the establishment of the Diffusion-Fundamentals conference series with an associated online journal (Diffusion Fundamentals Online [77]). With its focus on diffusive spreading in nature, technology and society quite in general [78] guest diffusion in nanoporous materials continued to be a hot topic at these conferences. The involvement of several key persons in the field as local conference chairmen, including Stefano Brandani in 2007 [79], Doros Theodorou in 2009 [80], Marc-Olivier Coppens in 2011 and Jürgen Caro in 2015 [78] notably contributed to this development. Therefore, it is no surprising that, following first meetings on the fringes of the International Zeolite Conference and the Fundamentals of Adsorption conference, it was mainly the discussions during the 8th Diffusion Fundamentals
We are now close to the completion of the first step in this project, namely the production of a thematic issue of the Adsorption Journal that may serve as a source for formulating the expected guidelines [81]. Most of the contributions are accessible via Adsorption, T.I.: Diffusion in Nanoporous Solids [82]. The upcoming Diffusion-Fundamentals IX conference in Krakow, September 2022 [83] is scheduled to serve as a forum for a detailed discussion of these contributions, aiming at their condensation to the guidelines expected to be formulated as a result of this IUPAC initiative. The present contribution is intended to contribute to the preparation of this discussion. Also, with the present contribution, we will try to follow Jens Weitkamp’s example who was always concerned that decisions of relevance should always be based on the input of experts.

3 The Various Views on Diffusion in Nanopores and their Reflection in the IUPAC Initiative

The perspective, under which mass transfer in nanoporous materials is considered, is a function of the mode of measurement. We will consider three possibilities as to how these different perspectives may be classified, with reference to the various techniques of measurement as presented in [81].

3.1 Microscopic vs. Macroscopic

There is a huge difference between the space scales of the elementary processes of diffusion and conversion in the nanoporous material as the elementary steps in matter upgrading, and the dimensions of the plants employed for their industrial realization and exploitation. Large differences in the length scales are already needed for characterizing the texture of the nanoporous material. They range from the pore diameters up to the sizes of the agglomerates and pellets to which the porous material is usually molded for its technical use.

The techniques of experimental measurement of molecular diffusion cover, by their very nature, quite different space scales. Correspondingly different are also the types of mass transfer that they are able to follow. Depending on the given purpose, each of these pieces of information may be of interest. A clear understanding of what a special measuring technique is able to reveal is, therefore, the prime prerequisites of its appropriate, target-oriented application. A first orientation may be based on a classification of the measuring techniques with reference to the diffusion path lengths that the molecules under study typically cover during the course of the experiment. Following refs. [26, 84], Tab. 1 provides such a survey for the various techniques of diffusion measurement compiled in [81].

Measuring techniques with their focus on the elementary processes of molecular propagation are referred to as sub-microscopic. They include the various techniques of solid-state NMR [85, 86] and quasi-elastic neutron scattering (QENS [87]).

Microscopic techniques are generally understood to allow the observation of molecular displacements within the individual crystallites/particles of nanoporous material under study. Their spatial resolution is, correspondingly, in the range of micrometers as a typical size of nanoporous crystals. Their most prominent representative is the pulsed field gradient (PFG) NMR technique [88, 89]. Its key information, the probability distribution of molecular displacements during an observation time of milliseconds to seconds, is based on the observation of incredibly large molecular ensembles (on the order of 10^10), in contrast to single-molecule tracking (SMT [90]), by which one is able to trace diffusion paths of the individual molecules. Changes in the

| Measurement | under equilibrium | under non-equilibrium |
|-------------|-------------------|-----------------------|
| Submicroscopic | Solid-State NMR [85, 86], Quasi-Elastic Neutron Scattering (QENS) [87] | Microimaging [91] |
| Microscopic | Pulsed Field Gradient (PFG) NMR [88, 89], Single-Particle Tracking (SPT) [90] | (Single-Crystal) Membrane Permeation [99] |
| Mesoscopic | Dynamic Light Scattering (DLS) [100] | Adsorption/Desorption Kinetics [92], Liquid-Phase Batch Kinetics [93], Column Breakthrough Dynamics [94], Zero Length Columns (ZLC) Technique [95], Frequency Response (FR) Technique [96], NMR Imaging (MRI) [97], X-Ray Computed Tomography (XCT) [98] |

Table 1. Classification of the various techniques of diffusion measurement with nanoporous host-guest systems with reference to the scale of observation (microscopic vs. macroscopic) and the conditions under which the measurements are (generally) performed (equilibrium vs. non-equilibrium).
concentration profiles of the guest molecules within the individual crystals (rather than the positions of the individual molecules) are the focus of microimaging [91].

The information provided by macroscopic techniques of diffusion measurement refers to the whole bed of nanoporous crystals/particles. Depending on the system under consideration this information may refer to quite different features of mass transfer. Attribution of the macroscopically observed features to their “microscopic” origin needs particular care. The spectrum of techniques applicable for this purpose includes uptake and release measurements with loose beds of particles [92], liquid-phase batches [93] and packed-bed columns [94], as well as their “variants” such as the zero-length column (ZLC [95]) and the frequency response (FR [96]) techniques. Macroscopic diffusion measurements are also possible via NMR imaging (MRI) [97] and X-ray computed tomography (XCT) [98].

In between micro- and macroscopic measurements, a couple of techniques are able to deduce their information from the mass transfer of the individual particle/crystallite, without being able to directly perceive their interior. These mesoscopic techniques of diffusion measurement typically include membrane permeation studies [99] with single crystals. Also, the information provided by dynamic light scattering (DLS [100]) refers to individual particles/crystals.

Classifications are prone to undue simplifications. A given technique of measurement may, correspondingly, under certain conditions happen to be more properly assigned to another category. This refers to, e.g., uptake and release measurements [92, 95, 96] if performed with only a small amount of adsorbent particles so that bed effects may be excluded. The thus attainable information may indeed be referred to as meso- rather than macroscopic. Vice versa, on considering, e.g., sufficiently large observation times, PFG NMR diffusion studies [88, 89] must, more properly, be referred to as meso- or even macroscopic rather than as microscopic techniques. It is, most importantly, a particular virtue of QENS [87] to monitor, under appropriate conditions, not only the elementary steps of diffusion but also their superposition over distances providing clear evidence of Fickian diffusion, i.e., on displacements over “microscopic” dimensions.

It is an important task of diffusion theory and molecular modeling to contribute to a proper interpretation and correlation of the diffusion data collected under various conditions, starting from the elementary processes of molecular propagation up to their long-range behavior [101]. Acceleration of mass transfer in hierarchically structured pore systems [20, 102] and its benefit for catalytic conversion is the topic of [103]. Here included is also a presentation of the options provided by the Thiele concept [23] to determine diffusivities by analyzing the effectiveness factor of a chemical reaction in a porous catalyst [104]. Refs. [105, 106] refer to the particular challenges of the observation and quantitation of transport resistances at interfaces, notably at the boundary between the nanoporous bulk phase and its surroundings (the “surface barrier”).

3.2 Equilibrium vs. Non-equilibrium

Diffusion is based on the random movement of the constituents of the system under consideration. This movement exists whether or not the system as a whole is in equilibrium. Experimental measurement of diffusion phenomena may be based on the observation of non-equilibrium phenomena and on correlating, via Fick’s laws, their rate with the underlying diffusive fluxes. Alternatively, there are also possibilities to measure molecular diffusion under equilibrium conditions. Tab. 1 makes such a distinction. It refers to those techniques that necessitate a non-equilibrium situation as non-equilibrium techniques, and to the remaining ones as equilibrium techniques. An introduction to the various possibilities of measurement and the resulting physical parameters may be found in [107] and their theoretical foundation and correlation in [101].

Note that equilibrium techniques may also be applied under non-equilibrium conditions. Typical examples include the application of PFG NMR [88] and SPT [90] during transient uptake and release, just as also during chemical conversion. Vice versa, also non-equilibrium techniques may be applied to determine parameters defined under equilibrium conditions. This is, in particular, the case in the tracer techniques where, instead of uptake and release, one is following the rate of exchange between differently labelled molecules (in general different isotopes of the same chemical compound) with one type initially in, e.g., the pore space and the other one in the surrounding gas phase [28, 108, 109].

Following Fick’s 1st law, the transport diffusivity (also referred to as Fickian, collective or chemical diffusivity) is defined as the factor of proportionality between a diffusive flux and the concentration gradient giving rise to it. Similarly, the self- (or tracer) diffusivity may be defined as the factor of proportionality between the flux of an (isotopically) “labelled” molecular species and its concentration gradient within a system of uniform total concentration (i.e., of “labelled” and “unlabelled” molecules). The thus defined self- (or tracer) diffusivity may also be shown to (completely equivalently!) result from Einstein’s famous diffusion equation (see, e.g., [107] or Sect. 2.1.3 of [26]) as the factor of proportionality between the molecular mean square displacement and (six times) the observation time. The ergodic theorem [110] implies that, under equilibrium conditions, the time and ensemble averages, i.e., averages taken over one and the same particle during subsequent time intervals or for many particles within the same time interval, yield identical mean values. This hypothesis has been experimentally proved for guest diffusion in nanoporous glass [111] by the combined application of SPT [90] and PFG NMR [88].

As a consequence of the mutual interaction between the guest molecules, the difference in the physical situations as considered under the measurement of transport and self-diffusion gives rise also to differences in the diffusivities. It is by this very reasoning that these differences should be
expected to vanish in the limit of sufficiently small concentrations, i.e., under conditions where the interaction between the guest molecules becomes negligibly small – and distinction between equilibrium and non-equilibrium conditions becomes anyway meaningless [112]. Exactly this behavior has been observed in comparative studies using uptake and PFG NMR [75] and microimaging [91, 113]. Refs. [91,113], moreover, refer to the exceptional case where it is found that the (different) loading dependences of the coefficients of self- and transport diffusion can be derived from the system’s equilibrium data, namely the adsorption isotherms. The prediction is based on the classical transition state theory [114], which may become applicable to determine the rate of mass transfer in nanoporous systems as soon as, for narrow-pore materials, the passage through the “windows” between adjacent cages becomes the limiting process [115–117].

The information provided by dynamic light scattering (DLS [100]) and quasi-elastic neutron scattering (QENS [87]) is based on internal fluctuations within the system. These fluctuations are known to be subject, according to Onsager’s regression theorem [118] (see also Sect. 10.2 and 10.3 in [26]), to the same dependencies as observable macroscopically. This concerns in particular the correlation between concentration gradients and diffusive fluxes following Fick’s 1st law. It is for this reason that, via DLS [100] and QENS [87], transport diffusivities can be determined with the host-guest system at (macroscopic) equilibrium.

3.3 Laboratory Conditions vs. Conditions of Technical Use

In addition to answering fundamental questions of basic research as emerging on considering molecular ensembles under the influence of solid surfaces, diffusion measurement with nanoporous host-guest systems follow the very practical concern of exploring the optimum conditions for their technological exploitation. Notably in view of this latter concern, the conditions of measurement are often aspiring to be as close as possible to those of their technical use. There exist a number of measuring techniques, which obey this concern by their very nature. They include permeation studies [99] and the measurement of uptake and release studies with loose beds of particles [92] and packed-bed columns [94].

With appropriate provisions, also most of the other techniques can be employed for the investigation of technologically motivated issues. This concerns, in particular, a decision about the limiting steps of mass transfer and their evaluation as a function of the time-on-stream in the industrial device. In this context, the message provided by PFG NMR [88,89] has proven to be especially informative. Examples of its benefit include the investigation of A-type zeolites [18] where the industrial process of pellet formulation was found to give rise to the formation of transport resistances on the external surfaces of the individual crystals (surface barriers [105]). The intensity of these barriers increased dramatically during time on stream while, most remarkably, the intracrystalline diffusivity of typical probe molecules remained, essentially, unaffected [15,119]. Surface barriers were found to be mainly caused by lattice collapse [120] and coke deposits [15] close to the external surface of the zeolite crystallites (see also Sect. 16.9.3 in [26]).

In addition to providing a great deal of information about mass transfer in nanoporous materials, NMR is ideally suited for the in situ observation of chemical conversion. It is this type of application, which found Jens Weitkamp’s particular interest. He was among the first to combine the information provided by NMR spectroscopy on diffusion and reaction in zeolites [121–123] and thus set the course for Stuttgart to become a world-wide recognized center for the application of NMR spectroscopy not only of nanoporous materials, but also for the in situ analysis of chemical reactions in porous catalysts [124–126].

Recording of the spatial distribution of the molecules involved in catalytic reactions and of their temporal dependence necessitates the combination of NMR spectroscopy with imaging techniques as presented and discussed in [97]. Similar information can be provided by the application of microimaging [91,127] via IR microscopy [91,127,128]. More extensive information about the process of catalytic conversion is provided by SPT [90], enabling monitoring of even the individual reaction path ways [129–131].

4 Conclusion

Mass transfer is among the most important processes that determine the economic viability of possible technical applications of nanoporous materials. This relevance is in remarkable contrast to the many deficiencies in our knowledge in this field. We have discussed some of the reasons that have contributed to such a situation, with a summary of the ongoing efforts and activities, carried out under IUPAC’s auspices to overcome these deficiencies. The appreciation of Jens Weitkamp’s contributions to this development was our special concern and a heartfelt obligation.

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