More Than Just a Random Walk?

by Jörg Kärger, Douglas M. Ruthven, and Rustem Valiullin

Owing to their potential for eco-friendly matter upgrading by molecular sieving and shape-selective conversion, nanoporous materials are among the pioneers of green chemistry. The performance of their application is often controlled by diffusion, *i.e.* the rate of mass transfer within these materials. This mass transfer, however, is rather complex and subject to numerous influences. Unambiguous diffusion measurement has thus remained a challenge to this day with errors in the interpretation of experimental data being all too common. The present feature reports the efforts of an IUPAC initiative to overcome these limitations.

1. An omnipresent phenomenon

Diffusion, meaning the random movement of objects, is an omnipresent phenomenon. The fact that it is a topic of scientific consideration can be traced back to Heraclitus of Ephesus and his „panta rei" (everything flows) in the sixth century BCE. Random movement may be observed with real objects, typically atoms and molecules, the constituents of matter. In fact, our understanding of diffusion is mainly based on the observation of atomic and molecular diffusion. These "conventional" diffusion studies have served as the main source for the development of theoretical concepts for the description of diffusion phenomena.

Diffusion, however, may also be observed with larger objects such as the spread of viruses as pathogens, of which we have become painfully aware during the current pandemic. However, random movement may even be observed with objects as large as plants and animals, *e.g.* during their "invasion" into novel biotopes. The complexity of such phenomena increases the difficulty of making reliable predictions.

We are presently witnessing this complexity worldwide with the spreading of the coronavirus pandemic—and it is particularly true for the spreading of non-physical objects, such as rumors, linguistic features, or jokes. The study of the extent to which these phenomena may, in some of their features, be reasonably well interpreted within the framework of "conventional" diffusion concepts is a fascinating topic of current research [1].

2. A process of economic relevance

Diffusion is an important step in the process of value enhancement in many areas such as metallurgy and semiconductor production. This holds, in particular, for matter upgrading by molecular sieving and/or shape-selective conversion in nanoporous materials (see, *e.g.,* chapters 10 and 11 of [1] and [2, 3]). Following an IUPAC recommendation [4], *nanoporous* is the term used for characterizing materials with pore widths up to 100 nm. More specifically, materials with pores up to 2 nm are called *microporous*, from 2 to 50 nm *mesoporous* and beyond that *macroporous*.

With pore sizes of typically the same order as the sizes of the molecules under consideration, microporous materials offer particularly favorable conditions for target-oriented separation and transformation of the guest molecules. This is a basic prerequisite for their resource-conserving and environmentally friendly use.

The left side of Fig. 1 shows, schematically, the principle of operation when using microporous materials for mass separation. It takes advantage of the fact that the critical diameter of one component (here shown in blue) is sufficiently large, thus allowing (if at all) only a very slow penetration into the zeolite, while the smaller diameter of the molecules of the other component (shown in green) results in their rapid capture. Hence, during "filling" of the bed of zeolites, the permeate contains an excess of the blue molecules. Subsequently, in a "rinsing" phase, the other component is provided in abundance. Performance, *i.e.* the gain in value-added (*i.e.* separated) products per unit time, increases with increasing adsorption and desorption rates. Transport acceleration, as a consequence, leads to productivity enhancement. Note that this principle becomes particularly important when the boiling points of the mixture constituents are close to each other so that separation by distillation, the method of common choice, becomes extremely energy- and cost-intensive.
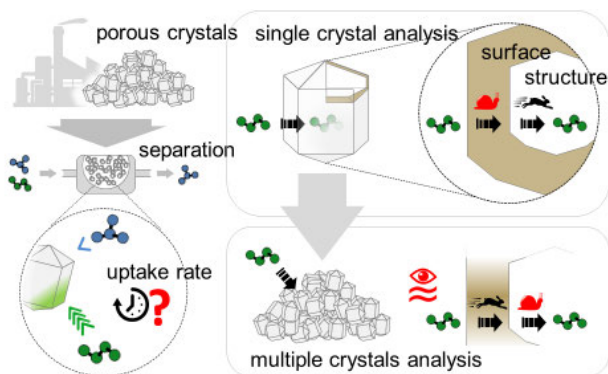

Figure 1: *Mixture separation by selective adsorption (after [5]). Left: Separation principle. Right: Example of misguided reasoning about the limiting process (see section 5 for details)*

With the widespread exploitation and extension of this principle, microporous materials, including zeolites as their economically most important representative, were, in the second half of the last century, among the first to foster "Non-Waste Technology and Production" and/or "Pollution Prevention", as a predecessor and promoter of today's "Green Chemistry" [6]. For example, the annual benefit worldwide from their exploitation in petroleum refining has been estimated to be at least 10 billion USD ([1] pp. 171/172).

As a matter of course, the gain in value-added products can never be faster than what is allowed by the rate of exchange between the interior of the microporous particles of the host material and their surroundings. This process of exchange includes, in particular, the rate of propagation (diffusion) of the guest molecules within the space of the micropores. The intimate contact between the guest molecules and the internal surface of the host material, which is a prerequisite for its functionality for matter separation and/or conversion results in a dramatic reduction in the mobility of the guest molecules. Ways out of this dilemma include the use of small particles or thin membranes, and of particles with a hierarchical pore structure where, ideally, the micropore space is traversed by a network of "transport" (i.e. meso- or macro-) pores.

Acceleration of mass transfer between the nanoporous material and its surroundings as a main route towards performance enhancement in their application in matter separation and conversion has to be based on the knowledge of all contributing processes and, notably, the assessment of their relative importance for overall mass transfer.

3. In search of the rate-determining step in mass transfer

For decades, it was assumed that the mitigation of mass transfer upon confinement in the micropores within the zeolite bulk phase would inevitably lead to the dominance of intracrystalline diffusion (also referred to as micropore, configurational or zeolitic diffusion) as the limiting process of molecular uptake and release by beds of zeolite crystallites. This was at least implied in experiments with sufficiently small beds of crystallites so that any significant resistance of mass transfer through the bed of crystallites could be excluded. Hence, over many years, rate measurements of molecular uptake and release were taken as the main source of information about intracrystalline diffusion.

It came, therefore, as a big surprise when the pulsed field gradient (PFG) technique of nuclear magnetic resonance (NMR, see, *e.g.*, [2, 3, 7] and chapters 10 and 12 of [1]) allowed the *direct* observation of molecular diffusion within the interior of the individual crystallites and, for a number of zeolitic host-guest systems, the diffusivities determined in this way notably exceeded the values deduced from uptake and release measurements with apparently identical zeolite specimens [8]. Uptake and release were thus shown, in many cases, to be controlled by processes other than genuine intra-crystalline diffusion.

It thus became clear that, in the study of sorption kinetics, it is necessary not only to determine the intra-crystalline diffusivity but also to establish the rates of other potentially rate controlling processes in order to assess their significance under the relevant conditions.

4. The "various diffusivities" and their measurement

Molecular uptake and release is, obviously, a consequence of the stochastic movement of the guest molecules upon entering or leaving the nanoporous particle. With Fig. 2a, under the influence of this random movement a concentration gradient is immediately seen to give rise to a diffusion flux j which is proportional to the concentration gradient (Fick's 1st law, eq. (1)), with the factor of proportionality D_T referred to as the transport (resp. collective, chemical or Fickian) diffusivity.

Random movement of molecules occurs, as a matter of course, also under equilibrium conditions. This may be investigated by considering, *e.g.,* a mixture of two isotopes (as indicated by the two shades of color in Fig. 2b) of essentially identical mobility. Then, in complete analogy with eq. (1), the flux j^* of either of the two isotopes may be noted as being proportional to the respective concentration gradients (eq. (2)). The factor of proportionality D is now referred to as the self- or tracer diffusivity.

In general, the coefficients of transport and of self-diffusion cannot be identical since the physical situations under which they are defined, are different. They do, however, coincide at sufficiently low concentrations, where the mutual interaction between different molecules becomes negligibly small.

With eqs. (1) and (2), the diffusivities may be determined by the measurement of fluxes either directly or by recording the *effect* of fluxes on considering, *e.g.,* uptake and release or, more generally, the variation in local concentration (Fick's 2nd law [1-3]).

There are also a number of techniques (including PFG NMR) by which it becomes possible to obtain information about the diffusion path of the individual molecules. In this case (Fig. 2c and eq. (3)) one is able to determine the coefficient of self- or tracer diffusion
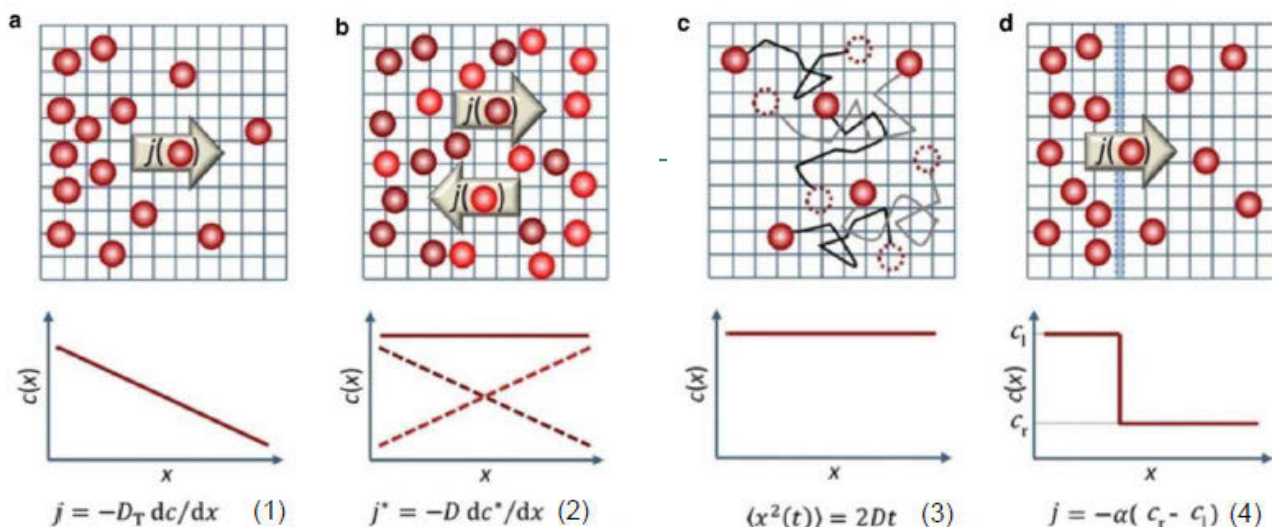
a
$$j = -D_T \, dc/dx \quad (1)$$

b
$$j^* = -D \, dc^*/dx \quad (2)$$

c
$$\langle x^2(t) \rangle = 2Dt \quad (3)$$

d
$$j = -\alpha(\,c_r - c_l\,) \quad (4)$$

Figure 2: *Definitions and conditions of measurement of the "various diffusivities" (reproduction of Fig. 1 in the Introductory paper by Kärger, Ruthven, Valiullin to [9])*

as the factor of proportionality between the observation time and the mean square displacement covered, during this time, by the molecule. In this proportionality, there appears an additional factor of 2 (4 or 6) for measurement of the displacement in one (two or three) dimensions. Coincidence of the definitions of the self-diffusivity by eqs. (2) and (3) is one of the messages of Einstein's famous diffusion equation [1-3].

Fig. 2d refers to the situation with additional transport resistances ("barriers") crossing the interior of the nanoporous particle. The permeability of these barriers is quantitated by their permeance, which is defined as the factor of proportionality between the flux through the barrier and the difference in the local concentrations on either side. For transport resistances on the particle surface ("surface barriers") one rather has to consider the difference between the guest concentration in equilibrium with the surroundings and the actual boundary concentration.

5. An example of misguided reasoning

Let us consider the two limiting cases in which molecular uptake and release is exclusively determined by intracrystalline diffusion (case of diffusion control) or by penetration through the surface barrier (barrier control). In these two cases, mass increase during molecular uptake or decrease during release follow different, well-defined time dependences. Analysis of the respective time dependences would, accordingly, be expected to provide immediate information about the limiting process in mass transfer.

One must have in mind, however, that the uptake curves are also affected by the crystal size and the intracrystalline diffusivity and/or the surface permeability (*i.e.* the intensity of the surface barrier), as well as by heat transfer. Hence, on considering uptake by a bed of crystals as the common scenario for, *e.g.,* *gravimetric* measurements of adsorption/desorption kinetics, the uptake curve results as only the sum of

various single-crystal uptake curves. The shape of the sum of these uptake curves, however, may be notably different from the shape of each individual one and may even, for a "suitable" distribution of the crystal properties, approach the other limiting case.

This is indeed the case on considering, *e.g.,* molecular uptake under barrier limitation with a bed of crystals with appropriately distributed surface permeabilities, but otherwise identical properties [5]. The right side of Fig. 1 refers, in a cartoon-like manner, to such a situation. Analyzing the time dependence of molecular uptake as recorded with a single crystal (top right) will correctly suggest that permeation through the crystal surface is the rate-determining process during uptake (when the guest molecules become "snails"). However, by using the same type of analysis, with beds of crystals (bottom right) intracrystalline diffusion will erroneously appear as the rate-determining step in the overall uptake.

This misinterpretation obviously results from the fact that the information provided by the experiment is still insufficient for a clear reflection of the transport phenomena taking place in the system. For the rate data to be quantitatively useful, the experiment must be designed in such a way that it will provide clear evidence concerning the rate limiting process.

6. A plethora of mechanisms and conditions

Section 4 already introduced two different ways in which diffusion phenomena become accessible by experimental measurement, namely via Fick's laws by recording molecular fluxes and/or the time dependence of molecular concentrations or via the Einstein relation by recording molecular mean square displacements. The distances over which, during the measurement, the molecules typically migrate are clearly a function of the applied method of measurement. This suggests, in addition to the above introduced distinction between equilibrium and non-equilibrium

measurement, a further, material-related classification of the measuring techniques. Thus techniques of diffusion measurement sensitive for displacements of the order of or smaller than the micropores are referred to as sub-microscopic, for displacements within the particle as microscopic and for displacements within the bed/pellet as macroscopic. Mesoscopic techniques are focused on a single crystal/particle without allowing a spatial resolution of its interior.

Table 1 provides a survey of the techniques which, so far, are in common use for studying molecular transport in nanoporous materials. The given classification cannot be more than a general guide. Deviations from the assessment include quasi-elastic neutron scattering which, under favorable conditions, allows the recording of displacements into the range of nanometers, and PFG NMR which, for sufficiently large observation times, is also applicable for macroscopic diffusion measurements. If performed with only a small amount of adsorbent particles the information attained by some of the techniques mentioned in the bottom 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-equilibrium techniques may be applied for studying diffusion under equilibrium conditions.

There are two more classification features that do not appear in table 1. 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 towards a certain molecular species is inherent to the technique, with other techniques selective diffusion measurement 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.

With this last example we are back to the "example of misguided reasoning" that we considered in section 5. Misguidance arose because we considered uptake by a bed of crystals rather than by a single crystal. It is true, however, that the option of making measurements with a single crystal might not be available. It is therefore important to be aware that, in the given situation, it is often possible to distinguish between diffusion and surface barrier control even from conventional uptake and release measurements. This option is provided by the so-called partial loading experiment which consists of an adsorption measurement followed, before saturation is reached, by a desorption experiment. A reduction of the time interval between these two experiments leaves, under barrier limitation, the (normalized) desorption curve unaffected while it becomes increasingly steeper under diffusion limitation (see Ruthven *et al.* in [9]).

Measurement	Equilibrium	Non-Equilibrium
Submicroscopic	Solid-State NMR Quasi-Elastic Neutron Scattering (QENS)	
Microscopic	Pulsed Field Gradient (PFG) NMR Single-Particle Tracking (SPT)	Microimaging
Mesoscopic	Dynamic Light Scattering (DLS)	(Single-Crystal) Membrane Permeation
Macroscopic		Adsorption/Desorption Kinetics Liquid-Phase Batch Kinetics Column Breakthrough Dynamics Zero Length Column (ZLC) Technique Frequency Response (FR) Technique NMR Imaging (MRI) X-Ray Computed Tomography (XCT)

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"). These techniques are in the focus of the activities of an IUPAC task group that has been established for providing a "comprehensive set of guidelines for measurements and reporting of diffusion properties of chemical compounds in nanoporous materials". Details of the various techniques are presented in a Thematic Issue of the Adsorption Journal [9]. Following preceding versions, such as those in [3], the table is adapted from [10], where also complete citations for the table entries may be found.*

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7. The random walk of diffusion research

In view of the variety of influences and the limitations in the significance of each of the measurement techniques as appearing from table 1, it is not surprising that the literature of this subject is replete with contradictory statements on mass transfer in nanoporous materials. This tendency is further exacerbated by the fact that nanoporous materials are often far from inert. Their structure and composition are known to be highly sensitive to the conditions of synthesis, storage and pretreatment. They may vary, furthermore, during their technical application and may even change during their preparation for the diffusion measurement and during the diffusion measurement itself.

All these changes, as a matter of course, affect the mass transfer within the systems. Most importantly, however, various constituents of mass transfer may be affected quite differently. This refers, *e.g.,* to an inhibition of mass transfer in either the microporous bulk phase or through surface barriers as discussed in sections 5 and 6. Examples of such seemingly contradictory studies may be found in the text books [2] and [3]. Recording of the "apparent" diffusivities attained in such studies might thus sometimes appear as a random walk on its own.

8. Wanted: A set of guidelines for diffusion measurement

Quantification of the various aspects of mass transfer, as appearing from table 1, necessitates the use of a wide range of different experimental techniques which are only accessible in an extended collaborative network. In 2015 an IUPAC task group dedicated to "Diffusion in Nanoporous Solids" (https://iupac.org/project/2015-002-2-100) has come together for the launch of such an activity, with its final goal "To provide a first comprehensive set of guidelines for measurements and reporting of diffusion properties of chemical compounds in nanoporous materials serving for catalytic, mass separation and other relevant purposes." As a first step, the group initiated the launch of a Thematic Issue of the Adsorption Journal [9] dedicated to the measurement of guest diffusion in nanoporous host materials.

This issue, which has just appeared, will serve as a basis for a first draft of what this "comprehensive set of guidelines" should look like. As a highlight in this discussion, we are happy to invite researchers in the field to attend the upcoming 9th Diffusion-Fundamentals Conference in September 2022 in Krakow, Poland (Diffusion Fundamentals IX - Diffusion Fundamentals - Faculty of Physics, Astronomy and Applied Computer Science (uj.edu.pl)) where a special workshop will be dedicated to the discussion and finalization of these guidelines. 🌐

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