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QENS and the Benefit of Diffusion Measurements over Different Length Scales

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Abstract

The quasi-elastic neutron scattering (QENS) technique was first used to derive self-diffusivities of hydrocarbons in zeolites, but transport diffusivities of deuterated molecules and of molecules which do not contain hydrogen atoms can now be measured. The technique allows to probe diffusion over length scales ranging from an Å to hundreds of Å. The mechanism of diffusion can thus be followed from the elementary jumps between adsorption sites to Fickian diffusion. Since the space and time scales of the neutron techniques match closely the ones covered by molecular simulations, one expects, and usually finds, good agreement between neutrons and simulations. The neutron data give therefore reference values, so that lower values obtained by other techniques measuring diffusion over longer length scales have to be explained by additional transport barriers.

Keywords: neutron scattering, zeolites, diffusion, *n*-alkanes

1. Introduction

The constant amelioration of the neutron instrumentation and of theoretical models provides unprecedented insights into the structure and dynamics of the framework and of adsorbed molecules, at the atomic and molecular level. The neutron application which is of concern here is quasi-elastic neutron scattering (QENS), which allows to characterize the translational and rotational motions of adsorbed molecules.

The diffusion of molecules in porous media can be studied by a large variety of methods [1]. Pulsed-field gradient (PFG) NMR and incoherent QENS measure the self-diffusivity, D_s , at thermodynamic equilibrium. Since hydrogen has the largest neutron incoherent cross-section, the first neutron measurements concerning diffusion in zeolites dealt with hydrogenated molecules.

In separation or catalytic applications, it is the transport diffusivity, D_t , which matters (this quantity is also named Fickian or chemical diffusivity). Transport diffusivities are traditionally measured under non-equilibrium conditions. Fick's first law defines D_t as the proportionality factor between the flux and a concentration gradient

$$J = -D_t \nabla c \quad (1)$$

Despite extensive work in the last decade, large discrepancies still persist between the various experimental techniques which measure diffusion in zeolites. One of the difficulties is to compare self- with transport diffusivities. D_s and D_t have a different

concentration dependence and the relationship between the two quantities is in general complex [1]. Comparisons between PFG NMR, QENS, and molecular dynamics (MD) simulations could only be made in the past at the level of D_s . At equilibrium, one can now obtain experimentally D_t by measuring the coherent scattering from deuterated molecules and from molecules which do not contain hydrogen atoms [2]. From equilibrium MD simulations, one cannot derive D_t , but one can determine the corrected diffusivity, D_0 , which is a collective mobility. The transport and corrected diffusivities are linked by considering that the driving force for diffusion is the chemical potential gradient, and not the concentration gradient; one obtains

$$D_t(c) = D_0(c) \left(\frac{d \ln p}{d \ln c} \right) = D_0(c) \Gamma \quad (2)$$

where Γ is the thermodynamic correction factor. One approximation which can be found in the literature is to replace D_0 by D_s . However, the self, transport, and corrected diffusivities are only equal at zero concentration. All these diffusivities can have a different concentration dependence. Recently, different diffusivities have been measured by QENS; in several cases experiments were compared with MD simulations, as shown in part 2.1.

Another recent achievement with neutron methods is the extension of the time window to longer times using the neutron spin-echo (NSE) technique. Using combined instruments, it is possible to cover time scales ranging from a femtosecond to about a microsecond. Converting to diffusion coefficients, diffusivities down to $10^{-14} \text{ m}^2\text{s}^{-1}$ can now be measured so that the accessible range is the same as with PFG NMR (in both techniques, there is no upper limit for the diffusivity).

The length scale which can be covered by neutron techniques with ideal zeolite samples, having a perfect crystallinity, can be of tens of nm. However, the available zeolite crystals have usually defects which give a strong intensity at small scattering angles. For this reason, the maximum distance which can be probed is about 10 nm. On the other hand, this means that diffusion in commercial samples, with crystallites of diameter $1 \mu\text{m}$ or less, can be studied with neutrons.

2. Concentration dependence of diffusivities

QENS and MD simulations often show that transport diffusivities increase with increasing loading while the self-diffusivities decrease. For a comparison between different systems, it is appropriate to remove the influence of the thermodynamic factor and to discuss the collective mobility in terms of the corrected diffusivity (also called Maxwell-Stephan diffusivity).

In several macroscopic measurements, the corrected diffusivity D_0 is assumed or found to be independent of sorbate concentration (e.g. refs. 3-4). This approximation, usually called Darken approximation, seemed to be supported by nonequilibrium simulations on methane in silicalite, at 300 K [5]. However, it was later reported that the Darken approximation was indeed followed for methane in silicalite at 298 K, but less at higher temperatures [6]. Furthermore, a large deviation was noticed for carbon tetrafluoride at various temperatures [6].

Experimentally, $D_0(c)$ can be obtained from coherent QENS measurements by dividing $D_t(c)$ by the thermodynamic correction factor, Γ , derived from experimental or simulated adsorption isotherms, or from QENS intensities.

2.1. Carbon tetrafluoride in silicalite

The structure of silicalite, a crystalline form of silica, consists of straight channels interconnected by sinusoidal channels, both having a free diameter of about 5.5 Å. The concentration dependence of the transport diffusivity for CF₄ in silicalite, as computed from MD simulations, has been recently compared to QENS measurements [8].

Since CF₄ is a purely coherent scatterer, only the transport diffusivity can be obtained from the QENS experiments. The thermodynamic correction factors, used to derive the experimental corrected diffusivities, were determined from the simulated adsorption isotherms. From MD simulations, both D_s and D_0 can be computed, D_t is derived by multiplying D_0 by Γ .

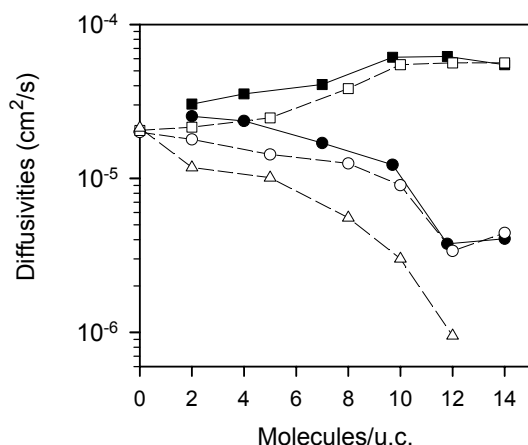


Fig. 1. Transport diffusivities (squares), corrected diffusivities (circles) and self-diffusivities (triangles) for CF₄ in silicalite at 200 K, as determined from QENS experiments (filled symbols) and atomistic simulations (open symbols).

The self, corrected, and transport diffusivities of CF₄ in silicalite are shown in Fig. 1, the QENS values as filled symbols, the MD values as open symbols. The agreement between experiment and simulation is remarkably good. When the loading increases, D_s decreases while D_t increases. The prediction from the simulations [6,7] that D_0 is not constant, but decreases strongly with increasing pore loading is confirmed by experiment [8]. Therefore, both simulation and experiment show that the Darken approximation is wrong for this system.

2.2. Concentration dependence of the corrected diffusivity

The concentration dependence of the self-diffusivity in zeolites has been extensively studied by PFG NMR [9]. Five different patterns were suggested, summarizing experimental data obtained for various molecules in different structures.

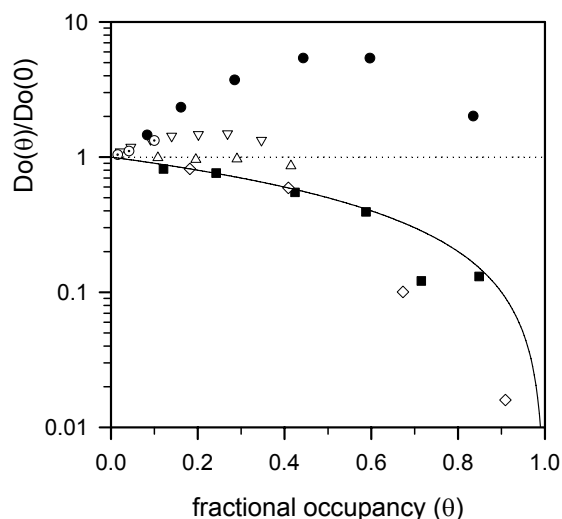


Fig. 2. Normalized corrected diffusivities obtained by QENS for several systems: (■) CF₄ in silicalite-1, (◇) benzene in NaY, (△) CO₂ in silicalite-1, (⊙) Ar in silicalite-1, (▽) N₂ in silicalite-1, (●) D₂ in NaX. The solid line gives the (1- θ) dependence, and the dotted line the “Darken approximation”.

The number of experimental or theoretical studies on the loading dependence of the corrected diffusivity is less than for D_s , but it is clear that neither the lattice gas model nor the Darken approximation can describe the loading dependence of D_0 in the various systems reported so far. This statement is illustrated in Fig. 2, which shows corrected diffusivities (normalised by $D_0(0)$ values) as a function of fractional occupancy for several systems. These data have been obtained experimentally by QENS, there is a good agreement with existing simulations [8,10]. Whereas the D_0 values for CF₄ in silicalite tend to follow a (1- θ) dependence [6-8], a neat maximum is observed for D₂ in NaX [2], and a small one for N₂ in silicalite [10].

3. Linear alkanes in silicalite

When some Si atoms of silicalite are substituted by Al atoms, protons or cations compensate the negative charges of the AlO_4^- tetrahedra, resulting in a material named ZSM-5. Both silicalite and ZSM-5 (structure code MFI) have found wide applications in catalysis or in the separation of gases and liquids. Zeolitic membranes, i.e. membranes where the zeolite is either deposited on or synthesised inside a ceramic support, are often based on the MFI structure.

The diffusion of alkanes in MFI-type zeolites is probably the system which has been the most studied by various experimental and theoretical methods. The magnitude of the diffusion coefficients in silicalite has been a point of controversy for about 20 years. The ‘macroscopic’ measurements yielding values which are orders of magnitude lower than those obtained by the ‘microscopic’ techniques: PFG NMR and QENS [1]. In the 1990s, a hierarchical simulation technique based on coarse-grained Brownian

dynamics and transition-state theory was performed on n -alkanes ranging from C_1 (methane) to C_{20} in silicalite [11]. No experimental data existed at that time for n -alkanes longer than C_6 . QENS measurements were performed later for chains up to C_{14} , but in Na-ZSM-5 zeolite [12], not in silicalite.

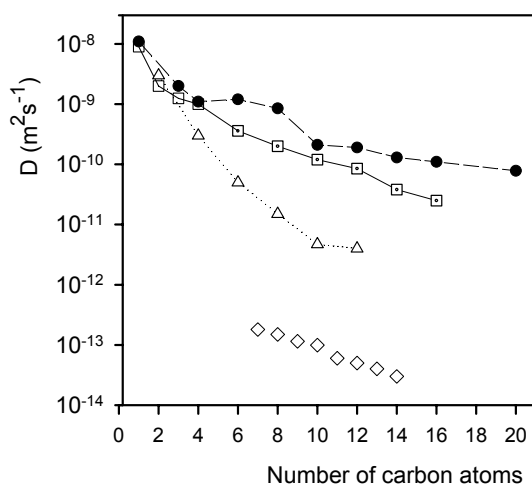


Fig. 3. Self-diffusion coefficients, obtained at 300 K by different techniques, for n -alkanes in silicalite: (●) hierarchical simulations [11], (□) QENS in ZSM-5 [12], (◻) QENS in silicalite [14], (△) PFG NMR [13], and (◇) ZLC [15].

The diffusion of n -alkanes in various MFI samples was recently revisited by QENS and PFG NMR [13,14]. The self-diffusivities are shown in Fig. 3 as a function of chain length.

The new QENS results obtained in silicalite are in much better agreement with the theoretical predictions than the previous QENS data measured with Na-ZSM-5. For C_{10} , the difference is now less than a factor of 2, which is negligible considering the experimental error on the QENS values and the error associated with the coarse-graining procedure in the simulations. That theoretical values are higher than QENS results is expected, because simulations are made in a perfect crystalline structure for an infinitely diluted sorbed phase. QENS measurements are performed on real crystals at a finite loading, corresponding to 12 carbon atoms per unit cell, and in this structure the self-diffusivity decreases with increasing loading.

Both techniques establish that the low-occupancy self-diffusivity is a monotonic function which decreases less than linearly with chain length. The activation energy for self-diffusion obtained from experiment and theory at low occupancy is around 5 kJ/mol for normal alkanes up to C_6 but rises with chain length beyond C_8 to approximately 15 kJ/mol for C_{16} . Molecular simulations relate this to the fact that alkanes longer than C_6 cannot fit entirely within channel segments and have to protrude into or straddle channel intersections, their translational motion requiring some degree of conformational isomerization [14].

In silicalite, QENS self-diffusivities are more than one order of magnitude higher than PFG-NMR diffusivities, for intermediate chain lengths. In other zeolite frameworks, the agreement between QENS and PFG NMR is generally better, even if the activation energy derived from PFG NMR is systematically larger. In Fig. 4, it can be

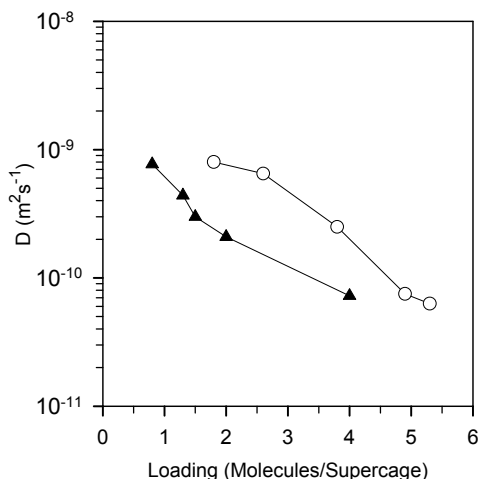


Fig. 4 Loading dependence of the self-diffusivities of benzene in NaX zeolite, at 468 K, obtained from (▲) QENS [16], and (○) PFG NMR [17].

seen that the self-diffusivities obtained for benzene in NaX zeolite from both techniques are within the same order of magnitude.

This shows the strong influence of intracrystalline barriers (defects, twinning, etc.) on molecular diffusion in silicalite. The PFG-NMR method, with its larger length scale of observation (μm), is more sensitive than QENS (length scale of several nm) to internal barriers in the crystal structure, if the distance between barriers is of hundreds of nm. The ZLC diffusivities in Fig. 3 are orders of magnitude lower than the ‘microscopic’ techniques. The ZLC measurements are performed with a thin bed of zeolite crystals so they are sensitive to all the defects (the influence of surface barriers could be ruled out). The presence of internal transport barriers within zeolite crystals is the most probable explanation for the discrepancies which have been reported in the literature for the past 30 years.

4. Linear alkanes in LTA zeolite, the ‘window effect’

LTA zeolite is part of numerous adsorption processes in the field of refining, petrochemicals or natural gas treatment. The structure consists of a cubic array of cages (diameter $\approx 11 \text{ \AA}$), interconnected by windows. In the calcium form, the effective diameter of the windows is close to 5 \AA , hence the product name: 5A. One of the most extensively used properties of 5A zeolite is the ability to adsorb linear alkanes while rejecting branched ones. This property is devoted to the production of highly branched $\text{C}_5\text{-C}_6$ paraffins for octane upgrading in gasoline or for supplying linear $\text{C}_{10}\text{-C}_{14}$ alkanes for linear alkylbenzene synthesis.

The diffusion of *n*-alkanes in 5A zeolite is too slow to be measured on conventional QENS instruments, but it is accessible by the neutron spin-echo (NSE) technique. Since coherent scatterers yield a better signal in NSE, deuterated *n*-alkanes were used for the measurements [18]. From the measured intermediate scattering functions, the diffusion

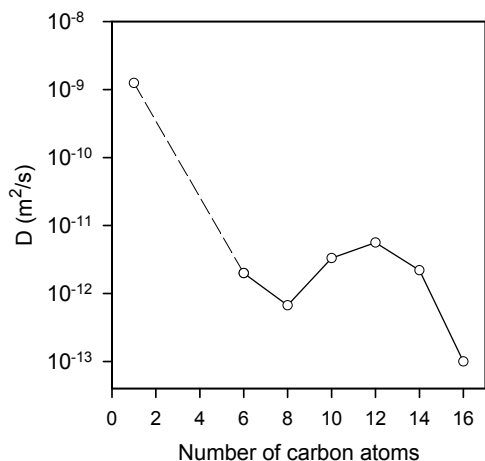


Fig. 5. Transport diffusivities obtained by NSE at 475 K for linear alkanes in 5A zeolite, as a function of the carbon number.

coefficients shown in Fig. 5 could be derived. One finds that the transport diffusivity has minima at C₈ and C₁₆ and a maximum at C₁₂. Since the loading was selected such that the number of carbon atoms per cavity stays constant (i.e. 12 C per α -cage), a similar maximum is expected for the corrected diffusivity, after correcting from the thermodynamic correction factor. The activation energy is lower for C₁₂, 35 kJ mol⁻¹, than for C₈, 41 kJ mol⁻¹.

These counter-intuitive results: a maximum in diffusivity as well as a minimum in activation energy for C₁₂, can be explained by the ‘window effect’. This term was coined by Goring to interpret anomalous transport results obtained in zeolite T, where he found that molecules in the C₁₂ range diffused about 2 orders of magnitude faster than those in the C₈ range [19]. However, the experimental conditions used by Goring have been criticized, and it is only recently that the concept of the window effect has gained some support. It provides an explanation for the NSE results: a C₈ molecule fits well into a cavity, whereas C₁₂ is too long to sit comfortably in a cage and adopts a conformation where one end of the molecule extends through a window. The energy barrier (largely entropic) is thus easier to cross for the longer molecule, leading to a higher diffusivity and to a lower activation energy.

Other measurements, performed by PFG NMR and ZLC techniques, also indicate an unusual diffusion behaviour for *n*-alkanes in 5A zeolite [15]. Self-diffusivities derived by PFG NMR indicate a shallow minimum in diffusivity at C₈ and a small maximum at C₁₀, although with a large experimental uncertainty. The transport diffusivity at low loading obtained from new ZLC measurements also shows a similar

trend, with a small minimum at C₁₁ and a small maximum at C₁₃-C₁₄. Even if the position of the maximum varies slightly and even if the order of magnitude of the diffusivities derived from the three methods is spread over three orders of magnitude, it is clear that the diffusion coefficient of C₈-C₁₆ in 5A does not decrease in a monotonous way, as it is the case in silicalite (v.s.).

5. Conclusion

In recent years, the diffusion coefficients derived from neutron methods for several molecules adsorbed in different zeolitic systems have been found to be larger than those obtained from the PFG NMR technique. Further, the activation energies reported from neutrons are often lower. These differences indicate that real zeolite crystals are different from the idealised views put forward by structural determinations. From the point of view of diffusion, most zeolite samples, notably silicalite but also LTA, do not represent homogeneous systems. The only explanation which can reconcile the different results is the presence of diffusion barriers within the crystals. If these defects occur on a length scale much larger than the diffusion path probed by neutrons, several nm, they will be of no influence on the diffusivities derived from this technique. Neutron diffusivities are thus expected to be close to simulations. On the other hand, PFG NMR which monitors displacements on the order of a micrometer will be sensitive to such barriers. Macroscopic methods, e.g. ZLC, will probe all the defects contained in the crystals and will therefore yield lower diffusivities.

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