

Application for Extension of Financial Support of

**Project 7:  
QENS Studies of Zeolitic Diffusion**

as part of a package of proposals  
aspiring joint support by CNRS, DFG, EPSRC and NSF

Dr. Hervé Jobic  
Institut de Recherches sur la Catalyse  
CNRS, Villeurbanne

Financial support requested from: CNRS

# 1. General Information

## 1.1. Applicant

Dr. Hervé Jobic  
Institut de Recherches sur la Catalyse,  
2 Avenue Albert Einstein,  
69626 Villeurbanne  
France  
Phone: (33) 472.44.53.01  
Private address: 161 Chemin du Calice,  
01120 La Boisse

## 1.2. Topic

QENS Studies of Zeolitic Diffusion

## 1.3. Code Word

Diffusion by QENS

## 1.4. Research Areas

Material Sciences,  
Chemical Engineering  
Physical Chemistry  
Interface Sciences

## 1.5. Scheduled Total Duration of Support

six years

## 1.6. Period of Support Applied for

three years

## 1.7. Total Period of Support

support started in January 2003 as part of a CNRS/DFG bilateral proposal, jointly with Prof. Dr. Jörg Kärger, member of the research group, extension requested starting from November 2006

## 1.8. Summary

The unique position of QENS within the research group results from two outstanding abilities, viz. (i) to allow the simultaneous determination of transport diffusivities, self-diffusivities and of the thermodynamic factor, which - by combination with the transport diffusivity - yields the so-called corrected diffusivity and (ii) to be able to follow the propagation pattern of guest molecules starting from distances of tens of nanometers down into the range of the elementary steps. Owing to the first option, QENS data may be simultaneously compared with both equilibrium techniques like PFG NMR and (T) ZLC and non-equilibrium techniques like uptake/release, FR, ZLC, single-crystal permeation and

IR/interference microscopy. Moreover, like PFG NMR, QENS as well allows the investigation of multi-component diffusion. The second option makes QENS very insensitive to the impairing influence of failures in the zeolite structure like internal transport barriers. As a consequence, QENS data on molecular diffusion in zeolitic host guest systems should serve as the most reliable target for attempts to simulate this processes by molecular modelling. The application of QENS to the host-guest systems envisaged by the research group will particular concentrate on the outmost exploitation of these particular options.

## **2. State of the Art, Own Activities in the Field**

### **2.1. State of the Art**

The constant amelioration of the neutron instrumentation and of the theoretical models provides unprecedented insights into the dynamics of the framework and of adsorbed molecules, at the atomic and molecular level. Using combined instruments, it is possible to cover energy transfers ranging from a few neV to hundreds of meV, corresponding to time scales from about a microsecond to a femtosecond.

Pulsed-field gradient (PFG) NMR and incoherent quasi-elastic neutron scattering (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. Until recently, the figure quoted in the literature for the lowest diffusivity accessible by QENS was  $10^{-12} \text{ m}^2\text{s}^{-1}$ . The use of the neutron spin-echo (NSE) technique allows to measure diffusivities down to  $10^{-14} \text{ m}^2\text{s}^{-1}$ , so that the range of diffusivities is now exactly the same as with PFG NMR ( in both techniques, there is no upper limit for the diffusivity). The space 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 commercial samples, with crystallites of diameter 1  $\mu\text{m}$  or less, which are hard to investigate reliably with other techniques of diffusion measurement, can be easily studied with neutrons.

With the high-flux instruments that are available at the Institut Laue-Langevin, in Grenoble, it is possible to measure the scattering of deuterated molecules and of molecules which do not contain hydrogen atoms. These elements have mainly coherent cross sections, so that one can follow collective motions through pair correlation functions. The response can also be analysed in terms of the density autocorrelation function. By following the density fluctuations which occur at equilibrium, one can derive the transport diffusivity. In all other techniques, transport diffusivities are obtained under (macroscopic) non-equilibrium conditions.

### **2.2. Own Activities in the First Period**

The previous neutron scattering experiments were essentially performed to derive self-diffusivities of hydrogenated molecules in zeolites. In recent years, transport diffusivities of deuterated molecules and of molecules which do not contain hydrogen atoms, e.g.  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CF}_4$ , have been measured.

An anomalous transport effect was observed while measuring by neutron spin echo the diffusivity of linear alkanes in 5A zeolite: a minimum at  $\text{C}_8$  and a maximum at  $\text{C}_{12}$  were

found [1]. Further, the activation energy for diffusion is lower for  $C_{12}$  than for  $C_8$ . While in other zeolites the diffusivity decreases with increasing chain length, i.e. with increasing molecular mass, in a zeolite with cavities separated by small windows like in 5A, the entropic barrier may be more easily overcome by a longer chain which has one end protruding into a window. Hence the diffusivity of a long n-alkane can be larger and its activation energy can be lower compared with a shorter n-alkane. The neutron findings were confirmed by the unusual results obtained by other techniques for this system, by other members of the consortium [2].

A strong confinement effect was put into evidence when comparing the dynamics of n-hexane in 5A and in silicalite [3-5]. In MFI (silicalite-1 or ZSM-5), the molecule sits in channel segments and jumps from one channel to the next, avoiding the intersections. The energy barrier between adjacent adsorption sites is small: 5 kJ/mol so that the residence time inside a channel segment is very short:  $2 \times 10^{-10}$  s at 300 K. In 5A zeolite, n-hexane is adsorbed in the  $\alpha$ -cages, the barrier between adjacent cages is larger, 28 kJ/mol, so that the molecule spends a longer time exploring the volume of the cage. The residence time inside an  $\alpha$ -cage is  $2 \times 10^{-5}$  s at 300 K, which is 5 orders of magnitude longer than in MFI.

The collective mobility has been measured by neutron scattering techniques for the first time. The experimental values obtained for  $N_2$  and  $CO_2$  in silicalite were found to be in excellent agreement with molecular dynamics (MD) simulations [6, 7]. The concentration dependence of the corrected diffusivities was modelled taking into account the adsorption sites and the intermolecular interactions. From these results, as well as those obtained for other systems [8-10], the Darken approximation, which consists in considering that the corrected diffusivity does not vary with sorbate concentration, was shown to be invalid.

The thermodynamic correction factor can be evaluated from coherent neutron scattering data, by determining the structure factor,  $S(Q)$ , at low wave vector transfers. In the case of simple Langmuir or dual-site Langmuir isotherms, good agreement was observed with the values derived from the adsorption isotherms and from CBMC simulations[11]. The neutron technique is the only one which is able to access this quantity when the measurement of the adsorption isotherm is difficult, because of high temperatures or pressures.

The recent experiments performed on linear alkanes in silicalite [12-14], confirm the existence of transport barriers within the zeolite crystals. The neutron diffusivities are close to simulations and about one order of magnitude larger than the PFG NMR values. The agreement between QENS and simulations reflects that the two methods probe motion over the same small (nm) length scales, while PFG NMR measures displacements over longer ( $\mu$ m) length scales and is therefore more sensitive to defects in the crystalline structure.

## 3. Issues and Working Programme

### 3.1. Issues

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 PFG NMR. Further, the activation energies reported from neutrons are always lower. These discrepancies 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, e.g. silicalite-1, 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. On the other hand, PFG NMR which monitors displacements on the order of micrometers will be sensitive to such defects. Clever experiments have to be devised to quantify the influence of these internal barriers.

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, and any deviation from these values has to be explained by additional transport barriers.

### 3.2. Working Programme

The planned experiments require a complex instrumentation coupled with a high neutron flux. At the time being, the international research centre in Grenoble, the Institut Laue-Langevin, is still the best place in the world to perform such measurements. Seven different instruments are available there, they cover different domains of energy resolution/momentum transfer. Depending on the system, applications have to be made to select one of these highly demanded spectrometers.

#### 3.2.1. LTA

A clear maximum in the transport diffusivity has been recently observed by neutron spin echo for linear alkanes in NaCaA zeolite: C12 diffuses by one order of magnitude faster than C8 and C16 at 436 K [1]. Only a small maximum was observed by PFG NMR and ZLC techniques. One could try to measure the self-diffusivity of the faster diffusing molecules by incoherent scattering, using a back-scattering spectrometer.

#### 3.2.2. Silicalite-1/ZSM-5

If one can vary the density of internal barriers in silicalite crystals, the distance between such barriers could be evaluated by neutron scattering, by measuring diffusivities at different temperatures and various time and space scales.

So far, n-alkanes up to C16 have been measured by neutron scattering. The diffusion of even longer alkanes could be followed by neutron spin echo.

#### 3.2.3. NaX

This is possibly the only system where a reasonable agreement has been found between PFG NMR and ZLC techniques [15]. This should be checked including this time neutron scattering. The thermal frequency response (TFR) method, which was also used in the

previous study, could be applied to this system through a collaboration with Dr. Vincent Bourdin, LIMSI, Orsay.

Since there is growing evidence for internal barriers in silicalite-1, joint neutron – PFG NMR experiments should be conducted on NaX crystals, which can be synthesised in big dimensions. The diffusion of linear and branched alkanes would be studied, to check if the diffusivities derived from both methods coincide or not. By selecting molecules with different kinetic diameters, the activation energy for diffusion would be modified, varying thus the sensitivity to internal barriers.

Mixtures, either of hydrogenated-deuterated hydrocarbons, or mixtures with rare gases which are very weak scatterers (e.g. Ar or Xe), can be studied in any zeolite structure.

### 3.3. References

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## 4. Financial Support

secured by CNRS

## **5. Requirements for the Success of the Application**

### **5.1. Team Members**

Frank Morfin (technician)

### **5.2. Cooperation with Other Scientists**

Collaborations with scientists of the Institute Laue-Langevin, Grenoble, to prepare and perform the neutron experiments.

### **5.3. Available Equipments**

Neutron cells of various geometries (flat, cylindrical or annular) to fit the instruments requirements. Some of these have an introduction system for in situ adsorptions.

### **5.4. Support from the Own Budget**

The neutron containers are designed and constructed at the IRC.

### **5.5. Further Prerequisites**

The institute offers the working places for the co-workers, applied for, as well as the necessary laboratories. The infrastructure of the institute allows the use of data-networks and computer systems free of charge.

## **6. Signature**

Lyon, June 19, 2006



Dr. Hervé Jobic