

Application for Extension of Financial Support of

**Project 6:  
PFG NMR Studies of Zeolitic Diffusion**

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# 1. General Information

## 1.1. Applicants

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## 1.2. Topic

PFM NMR Studies of Zeolitic Diffusion

## 1.3. Code Word

Diffusion by PFM NMR

## 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 Dr. Hervé Jobic, member of the research group, extension requested starting from November 2006

## 1.8. Summary

Being able to bridge the gap between the displacement range of tens of nanometers as accessible by QENS and that of the macroscopic techniques, which are unable to resolve intracrystalline mass transfer, PFG NMR has a key position within the research group. Based on the results attained during the first period, PFG NMR studies during the period of extension will be mainly dedicated to seven interrelated issues, viz. (i) the elaboration and exploitation of the new options to enhance the sensitivity of PFG NMR by combination with MAS and, as practical consequences of this technical progress, (ii) the extension of the range of diffusivities towards lower values (in particular for long-chain length n-alkanes in NaCaA and MFI, and for aromatics in NaX as key-systems for the consortium), (iii) outmost approach towards the space scale of QENS for quantitating the intensity and spacing of internal transport resistances in MFI, (iv) the quantitation of zeolite surface barriers, in particular in combination with the deliberate variation of their intensity, (v) selective (single-component) diffusion measurement in multi-component systems, (vi) measurement of the principle elements of the diffusion tensor in anisotropic systems and (vii) confirmation of ideal one-dimensional diffusion in zeolites with 1d channel structure, including the observation of single-file diffusion covering the relevant time regimes of both  $\langle x^2(t) \rangle \propto \sqrt{t}$  (for displacements far below the micrometer range) and  $\langle x^2(t) \rangle \propto t$ , respectively

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

### 2.1. State of the Art

The number of publications on diffusions in zeolites is steadily increasing and covers essentially all topics of the field including sophisticated theoretical approaches [1-9] in need of adequately reliable experiments, challenging projects considering technological aspects of zeolitic diffusion [10-15], novel principles of diffusion measurement [16-19], diffusion anomalies [20-27] and an overwhelming number of "new" systems to be investigated [28-39], including the risk of new misinterpretations as long as the "old" problems are still unsolved. More and more groups are going to apply also PFG NMR for these studies, including the option of selective diffusion measurement in multi-component systems [40-42]. In these studies [43-46] also our finding of time-dependent intracrystalline diffusivities in zeolites and the associated hypothesis of the presence of intracrystalline transport resistances [47-49] has been supported. In none of these studies, however, field gradient intensities comparable to those of our home-built PFG NMR diffusion spectrometers FEGRIS NT and FT could be produced, which limited all these studies to much larger displacements. It is true that displacements comparable to those attainable by our PFG NMR device may become accessible by NMR studies in the stray field of specially designed super-conducting magnets [50-52]. This possibility is purchased, however, by the exclusion of the option of multi-component diffusion measurements and by a dramatically reduced signal-to-noise ratio.

### 2.2. Own Activities in the First Period

Within the methodological work accompanying the project, the successful combination of pulsed field gradient (PFG) NMR and magic angle spinning (MAS) NMR to MAS PFG NMR [53] and the application of this novel measuring principle to zeolitic host-guest systems [54, 55] mean a real breakthrough in our efforts to qualify PFG NMR to a level which permits direct comparison with the results of the other standard techniques over a reasonable range of

systems (e.g. n-alkanes with varying chain lengths in zeolites NaCaA, MFI and NaX) and experimental conditions (loading and temperature), rather than in a few exceptional cases only and/or via temperature extrapolation. This finding is of particular relevance, since the so far commonly used procedure to improve the measuring conditions for PFG NMR, viz. temperature enhancement, was found to give rise to chemical reactions within the NMR sample tubes (even for systems like n-alkanes in MFI and NaCaA, which have been supposed to remain inert under the given conditions [56, 57]). These novel options have become particularly obvious most recently with the first PFG NMR measurements of the diffusion of a branched alkane (iso-butane) in silicalite-1 which have become possible by combination with MAS. A publication "Mixture diffusion in zeolites studied by MAS PFG NMR and molecular simulation" by M. Fernandez, R. Krishna, A. Pampel, J. Kärger, D. Freude is in preparation. Moreover, by considering two-component mixtures with n-butane, in these studies the dramatic influence of the iso-butane molecules on the n-butane mobility, starting with iso-butane loadings of about half a molecule per channel intersection, could be demonstrated - in complete agreement with predictions by molecular modelling [58].

Extensive PFG NMR measurements have been performed to match the results obtained by the other techniques of the consortium, in particular with n-alkanes in NaCaA and silicalite-1/ZSM-5. They include the important result that with increasing chain lengths in NaCaA the diffusivities are found to increase again [59], while in silicalite-1/ZSM-5 over a similarly large range of chain lengths (up to 12 carbon atoms) the diffusivities were found to decrease monotonically with increasing chain lengths [57, 60]. In all these studies, the measured diffusivities were the smaller, the more macroscopic the techniques were, i.e. they decreased in the sequence QENS, PFG NMR and ZLC. Since PFG NMR operated at its very limit no further information could be deduced from a variation of the diffusion path lengths. Therefore, it has to remain the task of further studies (with notably improved options of PFG NMR by combination with MAS NMR) to confirm or to falsify the assumption that this tendency might be a consequence of internal barriers.

Owing to the much more open pore system, such problems do not exist for the application of PFG NMR to n-alkane diffusion in NaX. First PFG NMR experiments with the zeolite material provided for the research group, with n-hexane and n-hexadecane as guest molecules, led to diffusivities on the order of the previously measured values [61], where for the longer n-alkane a pronounced increase of the diffusivity with decreasing observation time was observed. This might be considered as an indication that, like assumed for NaCaA and silicalite-1/ZSM-5, also the bulk phase of zeolite NaX is traversed by transport resistances.

Important progress has also been made with respect to the application of PFG NMR to quantitate surface permeabilities on zeolite crystallites. As a significant improvement of the conventional way to evaluate the intensity of surface barriers by combining the results of the so-called NMR tracer desorption technique with the genuine intracrystalline diffusivities [62], the new method is based on a comparison between tracer exchange and the effective intracrystalline diffusivity. A publication "Quantifying surface barriers on nanoporous particles by pulsed field gradient NMR" by M. Krutyeva, D. Tzoulaki, C. Krause, S. Vasenkov, J. Kärger, X. Yang, J. Caro is in preparation, see also [63]. In this way, with methane and ethane in zeolite NaCaA, for the first time a systematic study of the temperature dependence of surface permeabilities has become possible. Most remarkably, these permeabilities could be measured already for the as-synthesized zeolite crystallites, while after TEOS-treatment the surface permeability was so dramatically reduced that, even for methane and at the highest temperature accessible in our experiments (200 °C), no exchange

between the intracrystalline and intercrystalline phases could be observed during the time scale of the PFG NMR measurement (i.e. during some 100 ms).

With the Y-type zeolites synthesized for the consortium by the Stuttgart group [64], for the first time PFG NMR was able to provide direct evidence that zeolite dealumination scarcely affects the intracrystalline diffusivity of n-alkanes (as a consequence of the fact that the mesopores created during the dealumination procedure obviously represent inclusions rather than transport pores traversing the crystals) [65]. In this way the previous finding by our PFG NMR studies was nicely confirmed that it is the intra-particle rather than the intra-crystalline mass transfer, which represents the rate-determining step in FCC catalysis [66, 67].

First PFG NMR experiments with two different batches of cation-free LTA, as one of the possible target systems of the research group, provided by Avelino Corma, agreed in the evidence on the existence of internal barriers but disagreed in their quantitation [68]. Further progress in this direction again necessitates the improvement of the conditions for PFG NMR measurement.

### **3. Issues and Working Programme**

#### **3.1. Issues**

PFG NMR is applied to yield quantitative information on the (genuine) self-diffusivities and on (additional) transport resistances in both the zeolite bulk phase and the crystal surfaces over the largest possible parameter range. This includes temperature, loading and sample pre-treatment (with a deliberate affection of surface resistances), with an improvement of the option of direct comparison with the results of the other techniques and of their quantitative correlation. This project includes in particular the realization of a significant improvement of the performance of the PFG NMR measuring technique elaborated during the first period and the concerted application of this novel option together with the two available home-built spectrometers to the systems in the focus of the research group, with special concern on the unique options of PFG NMR

- to provide diffusivity data over a large spectrum of systems and experimental conditions,
- to bridge the gap between the macroscopic diffusion techniques and QENS
- to allow the quantitation of zeolite surface barriers
- to selectively measure (single-component) diffusion in multi-component systems
- to determine the principle elements of the diffusion tensor in anisotropic systems and
- to trace diffusion anomalies in 1d and particularly single-file systems

#### **3.2. Working Programme**

With this project, we apply for the option to accomplish the BRUKER spectrometers Avance 400 and 750 with the micro-imaging system Micro 2.5. The thus achieved reinforcement of PFG NMR, i.e. the inclusion of the option of MAS PFG NMR with strong pulsed field gradients, is quintessential for the success of our efforts to clarify the origin of the differences between the different techniques of diffusion measurement of nanoporous materials and to explore and to quantitate the phenomena and structural features leading to these differences. These options are of particular relevance for diffusion measurements of host-guest systems at low molecular mobility (which, in turn, are best suited for measurement by the macroscopic techniques) and the measurement of multi-component diffusion. Though, with the presently available option of MAS PFG NMR diffusion measurements with weak field gradient pulse intensities ( $g \leq 0.5$  T/m), we were able to demonstrate the benefit of this new method [53, 55]

the enhancement of the width of the field gradient pulses attainable in this way was impaired by the low gradient intensity, which is more than one order of magnitude smaller than the field gradient intensities attainable by our home-built device with ultra-high intensity field gradient pulses [69, 70]. It is the time integral over the magnetic field gradient pulses, i.e., roughly speaking, the product of pulse duration and amplitude, which has to be made the larger, the smaller the displacements are, in which one is interested. Therefore, the presently available device is unsuitable for the purpose of our research group.

With measurements using the in-house facilities of the BRUKER AG [54], however, we were able to show that this deficiency may be overcome by the use of a state-of-the-art microimaging system, in combination with MAS. In this way, in comparison with our present possibilities, the field gradient amplitudes may be enhanced by a factor of 5, corresponding to an enhancement of the spatial resolution by the same factor. This dramatic enhancement in resolution allows the measurement of much smaller diffusivities (in fact, of diffusivities smaller by close to two orders, since they scale with the square of the displacements). This improvement does in particular concern mixtures where the application of MAS NMR is indispensable. Simultaneously, the thus attained enhancement of resolution provides notably better options to fill the gap between the length scales of QENS and PFG NMR, as a central challenge of the present work. Much concern shall be spent, therefore, at the beginning of this project to methodological, explorative studies to fully exploit the options provided by the micro-imaging system which we apply for with the present project.

With respect to the host-guest systems considered by the research group, the focus of our (MAS) PFG NMR studies shall be on the issues specified in the following sections.

### **3.2.1. LTA**

As one of the most intriguing results obtained during the first period of support, coordinated measurements by PFG NMR, QENS and ZLC detected a pronounced deviation from a monotonic decay with increasing chain lengths for the n-alkane diffusivities in zeolite NaCaA [59, 71], in particular in the range from 7 to 12 carbon atoms. Since PFG NMR had to operate under limiting conditions of both the temperature scale (with the risk of chemical reactions) and spatial resolution, the information provided by us was by far not as precise as that provided by QENS and ZLC. Though the PFG NMR data resulted to appear intermediate between the (higher) QENS diffusivities and the (lower) ZLC diffusivities, it was impossible to fathom the origin of these differences by varying the observation time of the measurements. With the new options of MAS PFG NMR, future activities have to concentrate on this very issue, i.e. on the determination of the dependence of the intracrystalline diffusivities on the traced diffusion path length (striving to get to the range of QENS as closely as possible) over the largest possible temperature range and range of chain length. It is in particular the knowledge of the temperature dependence (and hence of the activation energy) of diffusion which is needed for the elaboration of an experiment-based, concise microdynamic model of molecular transport in zeolite NaCaA.

Choosing measuring conditions and guest molecules, which allow the observation of sufficiently large displacements, on the other hand, PFG NMR will as well be applied to directly determine the effect of a reduced permeability on the crystal surface (i. e., of the so-called surface barriers), which allows to discriminate between the intracrystalline transport resistances and those on the outer surface (including the finite rate of guest supply out of the gas phase). In this way, the effect of a deliberate variation of the intensity of surface resistances (e.g. by TEOS treatment - see project 1) and its variation with chain length and

temperature may be recorded. As a central issue of the research group, coinciding evidence of the different measuring techniques on these resistances has to be provided.

In this way, important additional experimental evidence is provided which has to be incorporated in search of the origin for the different patterns provided by the so far applied techniques (QENS, PFG NMR and ZLC) for the deviations from a monotonic decrease of the apparent diffusivities with increasing chain lengths.

Further, (MAS) PFG NMR diffusion studies shall be performed with methanol. Methanol in NaCaA was the first system, in which intracrystalline transport diffusion could directly be observed via interference microscopy [72, 73], owing to the pronounced effect of methanol loading on the optical density of the host crystals. Due to the presence of the bivalent calcium ions in the zeolite bulk phase, however, the intracrystalline diffusivity of methanol as a polar molecule is additionally slowed down, so that again (conventional) PFG NMR did not provide better results than a first estimate of the order of magnitude [72, 73]. Future MAS PFG NMR studies have to overcome this deficiency.

In cation-free LTA a dramatic enhancement of the intracrystalline diffusivity should be observed. This concerns in particular the polar methanol molecules, so that their diffusivities should get closer to those of methane and ethane. First PFG NMR studies of such material [68], however, suggest that in the specimens under study internal transport resistances rather than the zeolite bulk phase control their diffusion properties. The investigation of, hopefully more ideally structured, specimens of cation-free LTA shall remain an attractive task for the research group and in particular for PFG NMR. In addition to the convenience of this host system for molecular modelling, diffusion studies are particularly interesting since MD simulations suggest the occurrence of most striking diffusion anomalies, viz. decreasing bulk-phase diffusivities with increasing temperature [74].

Zeolite NaCaA represents an ideal model system for multicomponent diffusion studies by MAS PFG NMR. The measurements shall in particular include mixtures of small chain length (ethane, propane) and large chain length (n-hexane) n-alkanes. Following both the general predictions of irreversible thermodynamics [75] and the application of the Maxwell-Stefan formalism to zeolites [76, 77] in this case correlation between the single- and two-component diffusivities can be expected to be mainly mediated by the thermodynamic factor rather than by micro-kinetic correlations.

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

During the first period, in contrast to the findings with zeolite NaCaA, the diffusivity of the n-alkanes in MFI-type zeolites was found to decrease monotonically with increasing chain length [57, 60]. Similarly as with NaCaA, the results of PFG NMR, being intermediate between the QENS and the ZLC data, confirmed this general trend. However, as a consequence of limitation in the accuracy, PFG NMR was unable to contribute - e.g. by extended variation of the chain lengths, the observation times and the temperature - to a confirmation of the assumption that the observed trends have to be explained by the existence of internal barriers and their different influences on the measuring techniques considered. The application of MAS PFG NMR to overcome these deficiencies is among the crucial tasks within this project. Activities in this direction are additionally stimulated by the fact that in both previous single-crystal permeation studies [78] and simulations by molecular modelling [1, 4, 13], similarly as with zeolite NaCaA, also indications for oscillating diffusivities with increasing chain lengths have been observed. In addition, following our work within the first period [79], PFG NMR has to be further exploited to clarify the possible influence of

additional transport barriers on the crystal surfaces on the macroscopic techniques of diffusion measurement [80, 81].

In comparison with the n-alkanes, diffusion of branched n-alkanes and aromatics is notably reduced. With the aspired involvement of MAS PFG NMR with large field gradient intensities, for the first time such systems will become accessible by pulsed field gradient NMR. Both the practical impact of such studies and the option to directly trace the influence of compatibility ("commensurability") of channel architecture and molecular shape on diffusion [82-86] (with all the consequences for fundamental research) make such studies highly desirable. MAS PFG NMR will in particular contribute to this issue by the study of two-component diffusion, preferably with guest molecules vastly differing in their mobilities. In this way, the interrelation between the different diffusivities based on their microkinetic coupling (in addition to the omnipresent influence of (equilibrium) thermodynamics mediated by the two-component adsorption isotherms) is expected to appear in the most pronounced way. Moreover, in this way the mobility of one component (e.g. aromatics) which even by the application of MAS PFG NMR cannot be followed directly, may be traced by considering its influence on the second component.

It remains a particular challenge to trace and confirm the existence of those transport resistances with spacings in the  $\mu\text{m}$  range as detected by PFG NMR [47, 48]. They are considered to provide the explanation for the sequence in the magnitudes of the diffusivities, but the quantitative proof of this hypothesis is still missing. This means in particular that the extrapolation of the MAS PFG NMR data to small displacements should be shown to be comparable with the QENS data, and that their extrapolation to larger displacements should finally lead to the data of the macroscopic techniques, including the additional influence by surface barriers.

For comparison with the macroscopic techniques it is in fact sufficient to use only the information provided by PFG NMR for the mean diffusivity, represented by one third of the trace of the principal elements of the diffusion tensor. However, in comparison with the information potentially provided by the microscopic techniques and by single-crystal membrane permeation (and, moreover, in view of the option to distinguish between diffusion anisotropy in the related channel networks of zeolites MFI and MEL if the adequate zeolite samples are available) PFG NMR shall as well be used to deduce separate information about the principal elements of the diffusion tensor.

### 3.2.3. *NaX*

First PFG NMR studies with the material provided for the consortium satisfactorily reproduced the results of previous studies [61]. In addition, again a decrease of the PFG NMR diffusivities with increasing displacements became obvious. In addition to measurement of the chain length dependence of the n-alkanes in NaX in comparison with the data of the other groups, it is in particular this dependence of the diffusivities on the displacements which has to be in the focus of the studies. Again, MAS PFG NMR has to be applied to get access to the smallest possible spacings, ensuring best conditions for comparison with QENS and for the exploration of internal barriers. Most remarkably, with benzene and methanol as guest molecules, zeolite NaX was found to be a host system giving rise to either of the limiting cases, viz. of agreement (for methanol) and disagreement (for benzene), in comparative diffusion studies with macroscopic and microscopic techniques [87-89]. It is in complete agreement with this finding, that in our present studies the dependence of the diffusivities on the considered displacement was found to be in turn a function of the guest molecules



considered, their loading and the measuring temperature. The exploration of these interdependences and their correlation with the results of the different techniques represents one of the central tasks of our joint work. Since in previous studies the difference between the macroscopic and microscopic diffusivities of benzene/toluene in NaX was found to dramatically decrease with increasing loading the search of similar tendencies in the dependence of the PFG NMR diffusivities on the observed displacements is particularly intriguing.

As a wide-pore zeolite, NaX offers the best measuring conditions for the application of PFG NMR among the host systems considered. This concerns in particular the studies of multi-component diffusion, which shall be performed with special attention to mixtures of n-alkanes and aromatics as the standard guest molecules of the single component diffusion studies.

#### **3.2.4. Ferrierite**

Conventional application of PFG NMR to ferrierite is excluded by the small channel diameters which inhibit molecular reorientation. This leads to transverse relaxation rates in the range of hundreds of microseconds which excludes the application of sufficiently long ("wide") gradient pulses. Given the option of MAS PFG NMR which strong field gradients, it shall be checked whether the thus attainable enhancement of the width of the gradient pulses will already be sufficient to trace the relatively slow diffusion processes in such systems by (MAS) PFG NMR. However, even if such options turn out to exist, not more than but a tentative estimate of the intracrystalline diffusivities in such systems may be expected.

#### **3.2.5. AIPO<sub>4-5</sub>**

First PFG NMR measurements with AFI-type zeolites [90-92] were interpreted by the assumption of single-file diffusion. Though the considered host-guest system, in principle, may be expected to give rise to single-file diffusion, the dramatic differences between their ideal text-book structure and the experimental evidence provided in particular by interference and IR microscopy [93-96] require a critical reconsideration of these old measurements. Moreover, following the general guideline of this application, really reliable information can only be deduced by a concerted application of different measuring techniques. In fact, in these previous studies a comparison between the evidence of PFG NMR by different groups [90-92] as well as comparison between PFG NMR and QENS [97, 98] did lead to contradictory messages. While in transient experiments one-dimensional (including single-file) diffusion does not yield any peculiarities in comparison with multi-dimensional diffusion, the situation is completely different in self-diffusion experiments. In the latter case, molecular propagation is dramatically slowed down, resulting in the fact that molecular exchange with the surrounding scales with the third power of the file length (rather than with the second power as in the case of normal diffusion), and that, for displacements much shorter than the file length, the molecular mean square displacement increases in proportion to the root of the observation time, rather than to the time itself [99-103]. Most remarkably, with further increasing time the mean square displacement will again increase in proportion to the observation time itself, but now with a diffusivity reduced in comparison with the diffusivity of an isolated molecule by a factor, which is on the order of the maximum number of molecules which may be accommodated by the channel. The experimental observation of these different dependencies would confirm a remarkable feature of molecular confinement by single-file systems. The availability of really perfect crystals and of MAS PFG NMR are indispensable for these studies. In turn, the very PFG NMR measurements may provide direct information about the perfection of the crystals. The application of MAS in combination with

PFG NMR is needed in order to attain sufficiently large time intervals for both the application of the gradient pulses and observation. Finally, also for the first time, MAS PFG NMR studies of two-component diffusion with appropriately chosen molecular diameters would allow the observation of those phenomena of single-file diffusion, which have been referred to as dual-mode diffusion [104-107], including the option that the motion of one molecule is totally slaved by the mobility of a second component [108].

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## 4. Requested Financial Support

### 4.1. Personnel

As the central technique of the research group, PFG NMR has to operate at the limits of both the width and intensity of the field gradient pulses (maximum spatial resolution) and the observation time (minimum diffusivities). With the micro-imaging system we apply for a powerful means for a further extension of these limits in order to guarantee sufficient overlap (or at least better options for a mutual extrapolation) with the measuring conditions provided by the other techniques. This demanding task, in combination with the inevitability of a basic understanding of the chemistry of the systems under study, requires the employment of a post-doctoral fellow (Research Associate, BAT IIa). For performing a part of the measurements, funding of a research student (studentische Hilfskraft) is applied for.

### 4.2. Durable Equipments

Constituents of an NMR Micro-Imaging System (price quote is attached after page 17):

1.	Imaging Accessory including bay cabinet; gradient cooling BCU-20; GREAT control unit; Gradient amplifier (X,Y,Z) GRAT 60, 60 A; Control software ParaVision; Operating system upgrade for hard and software components; B <sub>0</sub> compensation unit and B <sub>0</sub> switching box GREAT/Z <sub>0</sub> for BSMS	€ 147,690
2.	Micro 2.5 wide bore gradient system	€ 26,000
3.	Components and basic parts for 400 MHz MAS probe	€ 13,600
4.	Installation	€ 13,946

All prices are without VAT, which is unknown for 2007.

### **Reasons for the Application for the NMR Micro-Imaging System**

Though the activities of the research group during the first period of the application package were notably promoted by the PFG NMR diffusion measurements, also the present limitations of this technique became obvious. They concern in particular (i) the measurement of low diffusivities, (ii) the resolution of small molecular displacements and (iii) the discrimination between different molecular species. All these options, however, are of crucial relevance for the success of the project:

(i) Since the diffusivities accessible by macroscopic techniques are limited towards high values, a further extension of the range of measurement by PFG NMR towards smaller diffusivities is inevitable to ensure a safe overlap of the messages provided by the microscopic and macroscopic technique.

(ii) In the systematic measurements of n-homologues in zeolites NaCaA and silicalite-1/ZSM-5 and first measurements with zeolite NaX, the diffusivities observed by QENS were found to be larger than the PFG NMR data, and these larger than the diffusivities observed by the macroscopic technique. The resulting message that the diffusivities are the smaller the "more macroscopic" are the measuring techniques, leads to the assumption that the intracrystalline space of the zeolites under study is traversed by transport resistances separated by distances of micrometers. The unequivocal confirmation of this assumption requires the observation of displacements much smaller than these distances. Furtheron, the observation of displacements far below the micrometer range is also quintessential for observing the  $\sqrt{t}$  dependence of the mean square displacement for single-file diffusion in zeolites.

(iii) With the measurement of multi-component diffusion and its correlation with the features of single-component diffusion, during the period of extension the research group is going to tackle an issue of relevance for both fundamental research and practical application. Both the dramatic reduction of the intracrystalline molecular mobility in comparison with the fluid bulk phase and sample heterogeneity (including heterogeneity in the magnetic susceptibilities) exclude the option of multi-component diffusion measurement by high-resolution PFG NMR.

During the first period we could demonstrate the successful combination of MAS NMR and PFG NMR for diffusion measurement in zeolites. This novel measuring principle, introduced to zeolite science and technology by our activities, overcomes the deficiencies of the conventional PFG NMR studies. With the options given at our institute, viz. an MAS PFG NMR facility with field gradient amplitudes of 0.54 T/m being more than one order of magnitude smaller than the gradient intensities provided by our purpose-built diffusion spectrometers FEGRIS 400 FT and NT, we could not do more than demonstrate and confirm the applicability of this novel measuring principle to zeolites. However, we have got the chance to directly explore the great potentials of this technique with a state-of-the-art micro-imaging system directly in the Bruker company, Rheinstetten, with field gradient intensities

of 2.6 T/m. The fact that also this value is still below the maximum field gradient intensities attainable in our purpose-built diffusion spectrometers, is by far overcompensated by the option of MAS PFG NMR to significantly enhance the time interval during which the field gradient pulses may be applied. Or saying it in other words: even the largest field gradient amplitudes are worthless if - as a consequence of the fast decay of transverse magnetisation - the time windows during which these pulses may be applied are too small. It is exactly the option of MAS, which notably enhances these time windows. In parallel, by the same mechanism, MAS effects a dramatic line narrowing, allowing the discrimination between different molecular species as a precondition for multi-component diffusion measurements.

The options provided by the micro-imaging system would also be of benefit for further DFG-supported projects of our faculty and of the faculty of Chemistry and Mineralogy, including, in particular, its use in the Dutch-German International Research Training Group "Diffusion in Porous Materials" (IGK 1056) and its application to diffusion studies of bio-membranes (PA 907/3-1)

#### **4.3. Consumables**

Special materials for probes (Teadid, Vespel, etc.)	€ 3,000
Fine chemicals as probe molecules in the PFG NMR studies	€ 3,000
Special glass tubes as containers for the (MAS) PFG NMR samples	€ 5,000

#### **4.4. Travelling**

Implying that the group meetings are ensured by central funding the travelling budget has primarily to be used for keeping personal contact with other laboratories, in particular in the field of NMR diffusion measurement and micro-imaging (Prof. Blümich, Aachen, Prof. Callaghan, Wellington) and for conference participation (Annual German Zeolite Conferences, International Conference on Magnetic Resonance in Porous Media, Conferences of the International Zeolite Association and Adsorption Association). Therefore, a total amount of 2000 € per year, corresponding to 6000 € for the total period of time, is requested for supporting visits and conference participation.

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

### **5.1. Team Members**

- a) Prof. Dr. Jörg Kärgner (applicant)
- b) Dr. Petrik Galvosas (applicant, Junior Professor)
- c) Prof. Dr. Dieter Freude (University Professor)
- d) Dr. habil. Frank Stallmach (senior researcher)
- e) Dr. Pavel Kortunov (post doc of the International Research Training Group),
- f) Dr. Margarita Krutyeva (separate DFG project)
- g) Dipl.-Phys. Cordula Krause (research technician)
- h) Lutz Moschkowitz (technician)

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

The primary partners of cooperation are the members of the consortium. With respect to methodical development, we shall maintain our close contact with Prof. emerit. D. Michel, Prof. J. Haase and Dr. A. Pampel (MPI for Human Cognitive and Brain Sciences) in Leipzig,



as well as with Prof. P. Callaghan, Wellington, and Prof. B. Blümich, Aachen.

### **5.3. Available Equipments**

- The purpose-built PFG NMR spectrometers for diffusion measurement with ultra-high-intensity field gradient pulses FEGRIS 400 NT and FEGRIS 400 FT
- The Bruker Avance spectrometers operating at 750 MHz and 400 MHz, to be complemented with the micro-imaging system applied for within this project for MAS PFG NMR

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

From the budget of the institute an amount of about 1000 € may be used for ensuring the operating conditions of the equipments.

### **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. Statements**

### **6.1. Collaborative Research Centres (Sonderforschungsbereiche)**

The present application cannot be part of any of the existing collaborative research centres of the University.

### **6.2. Application for Support by Different Sources**


We have never applied for financial support of this or a similar project. If we shall do so, we will immediately inform the German Science Foundation (DFG).

### **6.3. Information to the University Representative of DFG (Vertrauensmann)**

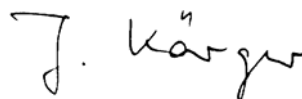
The university representative of the DFG, Prof. Dr. E. Hey-Hawkins, has been informed about this proposal.

## **7. Signature**

Leipzig, June 19, 2006



Dr. Petrik Galvosas



Prof. Dr. Jörg Kärger