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# Signals in Post-War Ruins, Five Orders of Magnitude and Pore Spaces Explored by NMR Diffusometry

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## Abstract

The 10th Bologna Conference on "Magnetic Resonance in Porous Media" was among the impressive events which, dedicated to the 600th anniversary of Leipzig University in December 2009, attracted colleagues from all over the world. The conference excursion took the participants to *Ferropolis*, a place north of Leipzig, equipped with impressive remainings of an old mining site, including huge conveyer bridges. Ferropolis also visualizes, in some way, Leipzig as a center of industry and science, with coal mining in its vicinity as one of the sources of industrial development and, hence, as a promoter of scientific progress. With pleasure I followed the invitation to talk on this occasion, by merging a plenary lecture with an after-dinner speech, about Leipzig's special affection towards the topic of the conference. This contribution is a reproduction of my talk, accompanied by most of the presented slides.

## Keywords

Leipzig, History, Diffusion, Zeolites, NMR

## 1. Views on Leipzig's History

### 1.2. A center of culture, science and technology

In December 2009 Leipzig celebrated the 600th birthday of its university. Besides Heidelberg, there is no other university in Germany which may look back on such a long time span of continuous activities in teaching and research. A most recent, detailed description of its history may be found in the special edition [1] dedicated to the anniversary. Some items on the history of Leipzig and its University – in particular in correlation with the topic of the conference - are contained in the booklet [2] shown on the introductory slide, figure 1, bottom right.

The front page of the booklet shows the new university building. You may take it as a symbol of the great cultural traditions in Leipzig's history. It commemorates the old university church, a church which survived World War II but which was, narrow-mindedly, destroyed afterwards. The church goes back to the 13th century. Here, with a sermon by Martin Luther, reformation started in Leipzig, and some of Johann Sebastian Bach's music, who was not only Cantor of the Thomas Church but also Director of Music of Leipzig University, were here performed for the first time.


10th Bologna Conference on

Magnetic Resonance in Porous Media

**Signals in post-war ruins,**
**five orders of magnitude**
**and pore spaces**
**explored by diffusion measurement**

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University of Leipzig
Faculty of Physics and Earth Sciences
Department of Interface Physics

Figure 1: Cover slide

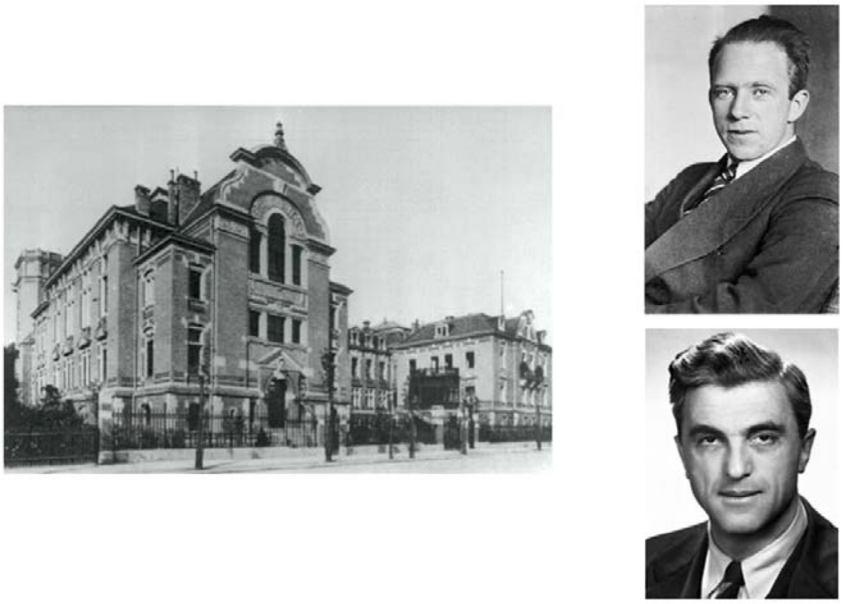
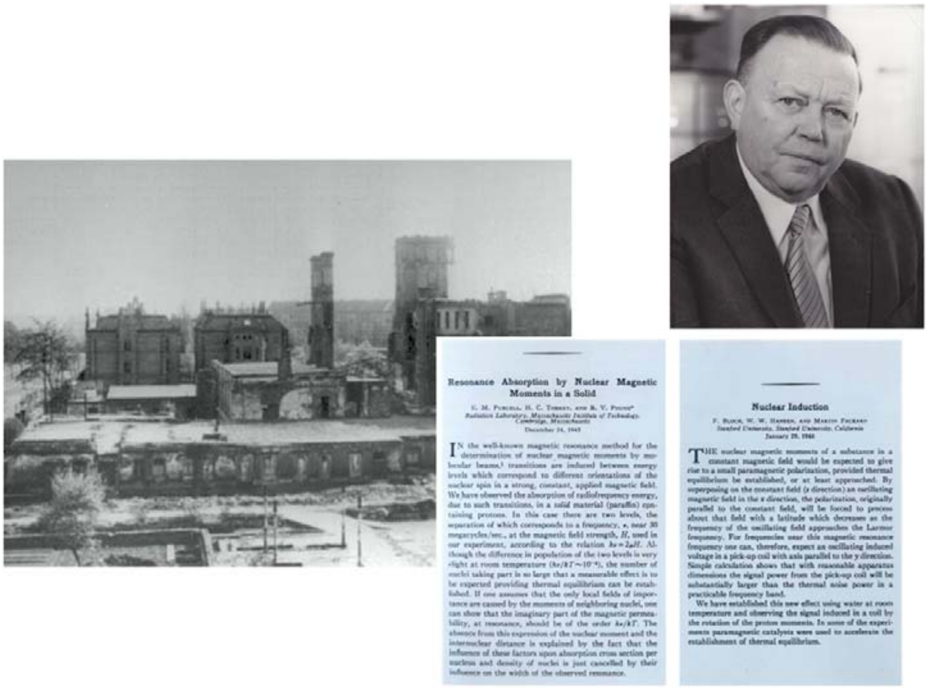


Figure 2: Leipzig's Institute of Physics built in 1905, with two of its celebrities, Werner Heisenberg (top) and Felix Bloch (bottom)

Similarly great was Leipzig's rank in science and so it happened that both Adolf Fick's and Albert Einstein's seminal papers on diffusion [3] appeared here in Leipzig (see Figure 1). The physics building, completed in 1905, the great "year of physics" owing to Einstein's seminal papers on quite different subjects, including his diffusion equation, is said to be among the worldwide most beautiful institutes of this time. It attracted, among many other prominent scholars, Werner Heisenberg (Figure 2). Soon he had with him a group of excellent young people. One of them was Felix Bloch.

We all are aware of the fatal developments in Germany in the beginning of the thirties and the terrible consequences. Many of the leading scientists left Germany, including Felix Bloch. Germany collapsed to ruins, both in a translated sense and in reality, like Leipzig's physical institute (Figure 3).



Resonance Absorption by Nuclear Magnetic Moments in a Solid

Nuclear Induction

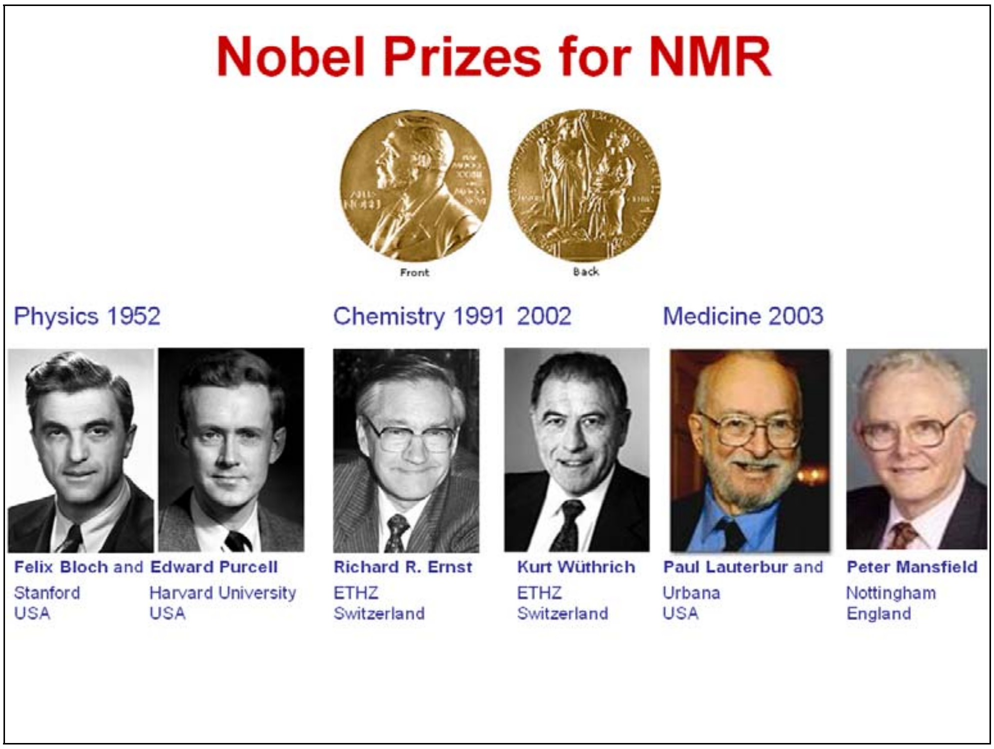
Phys. Rev. 69 (1946) 37 and 127

Figure 3: Ruins of Leipzig's Institute of Physics, the first papers on NMR and Artur Lösche who ensured the impact of these papers on science in Leipzig

## 1.2. Becoming the East Pole of Magnetic Resonance

With the collapse of the old regime, however, there emerged a new believe in the future, in particular among the young people who, after having served in the war, could now dedicate their activities to the benefit rather than the horror of mankind. It was around this time when Leipzig's physics department received a series of issues of Physical Reviews which were not delivered during the war [4]. They included also some papers on NMR which attracted the particular attention of Artur Lösche (Figure 3). These papers have led to the first Nobel prices delivered for achievements in a field which emerged in these days (Figure 4). Together with Edward Purcell we recognize the previous Leipzig PhD student Felix Bloch – and the continuing series of Nobel laureates indicates that the field continues to flourish into our days…

Here in Leipzig, Artur Lösche motivated his students to have a closer look at these papers and to reproduce the described experiments. As part of his diploma thesis, Harry Pfeifer (Figure 5) was able to successfully follow this advice: With the device shown in the figure he was the first to observe NMR signals in Germany and, most likely, even in the whole of Central Europe [5].


Nobel Prizes for NMR

Physics 1952
Chemistry 1991 2002
Medicine 2003

**Felix Bloch** and **Edward Purcell** **Richard R. Ernst** **Kurt Wüthrich** **Paul Lauterbur** and **Peter Mansfield**

Stanford
USA

Harvard University
USA

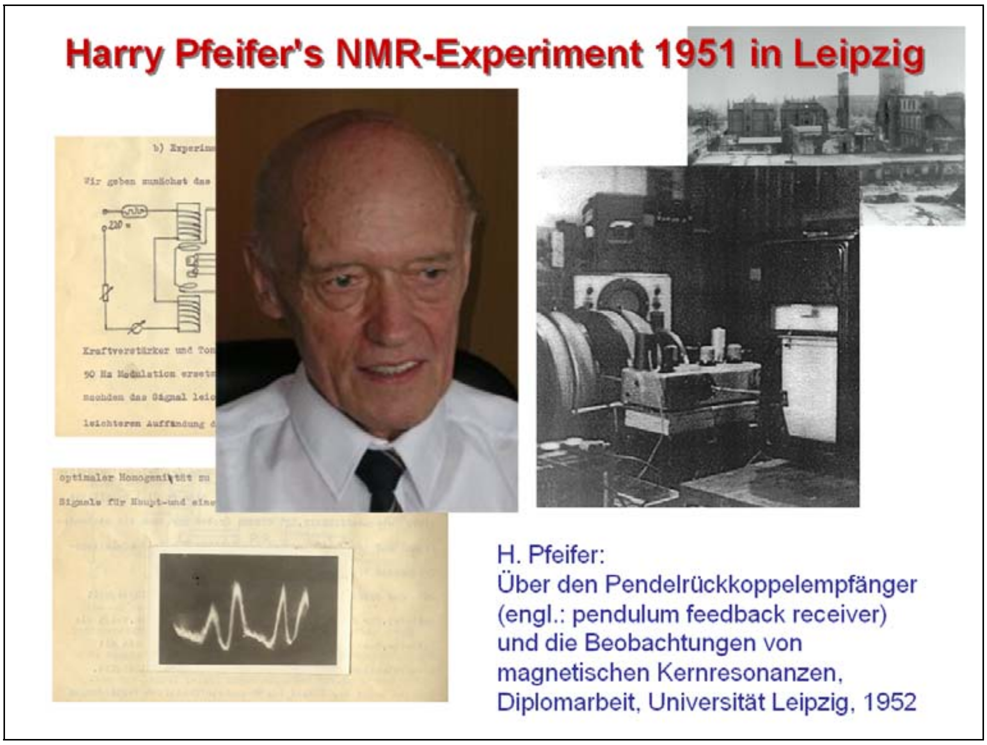
ETHZ
Switzerland

ETHZ
Switzerland

Urbana
USA

Nottingham
England

Figure 4: Awardees of Nobel Prizes in NMR


Harry Pfeifer's NMR-Experiment 1951 in Leipzig

H. Pfeifer:
Über den Pendelrückkoppelempfänger
(engl.: pendulum feedback receiver)
und die Beobachtungen von
magnetischen Kernresonanzen,
Diplomarbeit, Universität Leipzig, 1952

Figure 5: Harry Pfeifer and the first NMR signals in Central Europe

Ten years after the destruction of the old institute, the ruins have been replaced by a new physical institute (Figure 6). The painting shows it together with the old entrance columns and one of the old apartment houses for the professors where also Werner Heisenberg lived and which survived the bombardment. Our Japanese colleague and friend Taro Ito has made this painting after Germany's reunification which has enabled a thorough renovation of the

Figure 6: Main entrance to Leipzig's new Institute of Physics, completed in 1956. The painting by Taro Ito also shows the columns of the old entrance gate and the side wall of one of the old apartment houses belonging to the institute.

institute which has made it, once again, one of the most beautiful institutes in Germany. It is my particular pleasure to mention, in front of the magnetic resonance community, that this renovation is owed, to a most significant part, to Dieter Michel's activities (following, or better to say, in a break during his activities in the fields of NMR and ESR [6]) as the vice president of the council of the city of Leipzig after the peaceful revolution and, subsequently, as the Dean of our faculty.

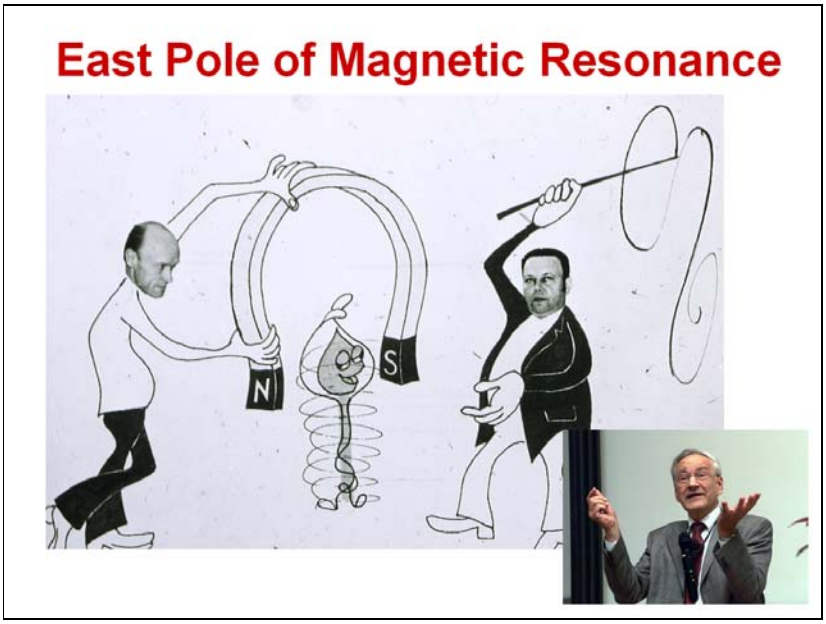

East Pole of Magnetic Resonance

Figure 7: Harry Pfeifer and Artur Lösche making Leipzig the East Pole of Magnetic Resonance, to which it has been referred by Richard Ernst during his talk in Leipzig in 1992

Benefitting from the functionality of the new physical institute, with a clear focus on NMR with its increasing spectrum of exploitation in material research, the activities of Artur Lösche and Harry Pfeifer and their groups made Leipzig an internationally accepted center of magnetic resonance, irrespective of numerous disadvantages and impediments associated with our location behind the iron curtain. Thus we took it as a particular appreciation to be referred to as the East Pole of Magnetic Resonance by Richard Ernst, the next one, following Purcell and Bloch, in the series of the Nobel Awardees, during one of his talks here in Leipzig (Fig. 7).

## 2. Revealing a Discrepancy of Five Orders of Magnitude

### 2.1. NMR with Zeolites: Top Research under Complicated Conditions

The five orders of magnitude referred to in the title of this contribution are closely related to my own work which I had the great luck and pleasure to start in Harry Pfeifer's group. Figure 8 shows him on a photograph in the center of his group made on the occasion of his 60th birthday in 1989 in front of our institute. One of the fields of research evolving in his group was the application of NMR to molecules adsorbed on solid surface. It was Horst Winkler who pioneered this research with his first paper on this subject here in Leipzig [7]. Soon Harry Pfeifer became aware of the twofold beauty which, in this respect, are offered by zeolites [8–10] (http://www.iza-structure.org/databases/), nanoporous crystalline solids with cavities which are so small that each of them may accommodate only a very small number of guest molecules (Figure 9). The thus realized intimate interaction of the molecules with the inner zeolite surface makes them an ideal system for both fundamental research and technological application, e.g. for petrol upgrading [11], with NMR often as the tool of choice for exploring elementary processes of diffusion and reaction [12,13].

Figure 8: Harry Pfeifer in front of the main entrance of the institute with his group on his 60th birthday in February 1989. Further on, in this report, are explicitly mentioned: Horst Winkler (first row, left in the figure), Dieter Freude (behind him, second row), Günter Seiffert (second row from top, left in the figure, behind Dieter Freude), Frank Stallmach (two rows just above Harry Pfeifer), Wilfried Heink (last row, behind Frank Stallmach)

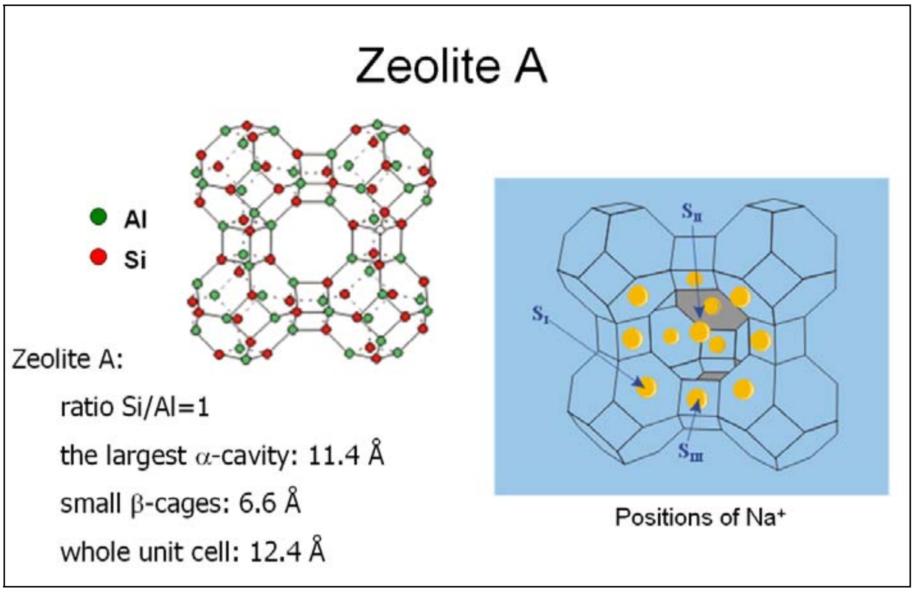
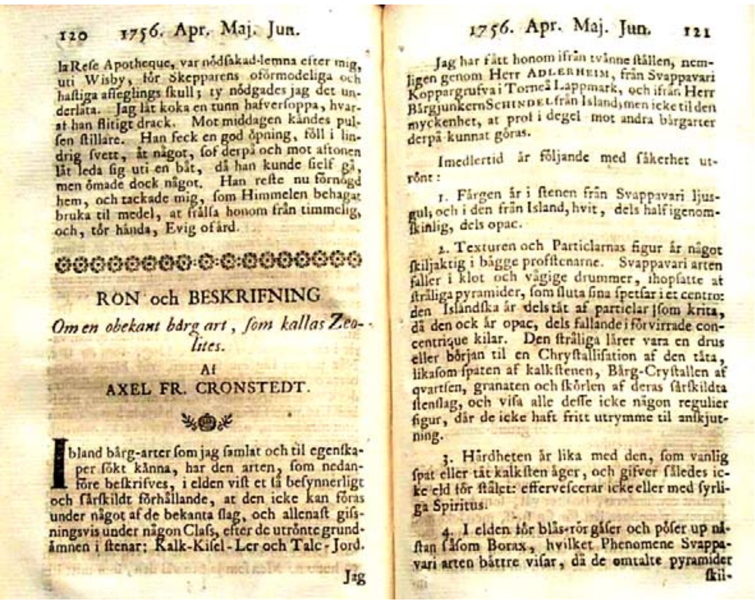


Figure 9: Structure of zeolites of type A with cation positions. Lines between vertices (i.e. positions of the aluminum or silicon atoms) represent their connections by an oxygen atom.



120 1756. Apr. Maj. Jun.

la Reſe Apotheque, var nödſakad-lemna efter mig, uti Wisby, för Skepparens oförmodeliga och haſtiga affeglings ſkull; ty nödgades jag det underlåta. Jag låt koka en tunn hafverſoppa, hvaraf han flitigt drack. Mot middagen kändes pulſen ſtillare. Han feck en god öpning, föll i lindrig ſvett, åt något, ſof derpå och mot aftonen lät leda ſig uti en båt, då han kunde ſielf gå, men ömade dock något. Han reſte nu förnögd hem, och tackade mig, ſom Himmelen behagat bruka til medel, at frålſa honom från timmelig, och, tör hända, Evig ofärd.

* * *

RON och BESKRIFNING

*Om en obekant bårg art, ſom kallas Zeolites.*

Af

AXEL FR. CRONSTEDT.

Ibland bårg-arter ſom jag ſamlat och til egenſkaper ſökt känna, har den arten, ſom nedanföre beſkrifves, i elden viſt et ſå beſynnerligt och ſärſkildt förhållande, at den icke kan föras under något af de bekanta ſlag, och allenaſt giſsningsvis under någon Claſs, efter de utrönte grundämnen i ſtenar: Kalk-Kiſel-Ler och Talc-Jord.

Jag

1756. Apr. Maj. Jun. 121

Jag har fått honom ifrån tvänne ſtällen, nemligen genom Herr ADLERHEIM, från Svappavari Koppargrufva i Torneå Lappmark, och ifrån Herr Bårgjunkern SCHINDEL från Island, men icke til den myckenhet, at prof i degel mot andra bårgarter derpå kunnat göras.

Imedlertid är följande med ſäkerhet utrönt:

1. Färgen är i ſtenen från Svappavari ljusgul, och i den från Island, hvit, dels half igenomſkinlig, dels opac.

2. Texturen och Particlarnas figur är något ſkiljaktig i bägge profſtenarne. Svappavari arten faller i klot och vågige drummer, ihopſatte af ſtråliga pyramider, ſom ſluta ſina ſpetſar i et centro: den Isländſka är dels tät af particlar ſom krita, då den ock är opac, dels fallande i förvirrade concentrique kilar. Den ſtråliga lärer vara en drus eller början til en Chryſtalliſation af den täta, likaſom ſpaten af kalkſtenen, Bårg-Cryſtallen af qvartſen, granaten och ſkörlen af deras ſärſkildta ſtenſlag, och viſa alle deſſe icke någon regulier figur, där de icke haft fritt utrymme til anſkjutning.

3. Hårdheten är lika med den, ſom vanlig ſpat eller tät kalkſten äger, och gifver ſåledes icke eld för ſtålet: efferveſcerar icke eller med ſyrliga Spiritus.

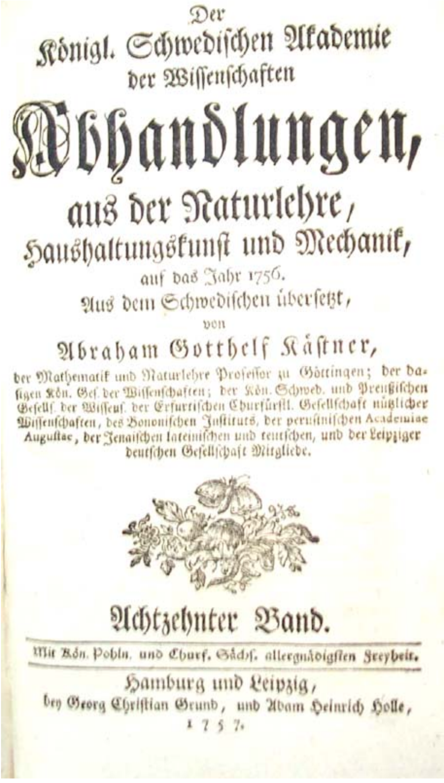
4. I elden för blås-rör gäſer och pöſer up näſtan ſåſom Borax, hvilket Phenomene Svappavari arten bättre viſar, då de omtalte pyramider

ſkil-

Figure 10: First publication on zeolites by Axel von Cronstedt in the Proceedings of the Royal Swedish Academy of Sciences in 1756

Zeolite research in Leipzig may be said to have benefitted from a coincidence which, once again, nicely characterizes Leipzig as a city of sciences. The very first publication dealing with zeolites appeared in the proceedings of the Swedish Academy of Sciences in 1756 where von Cronstaedt reported about the discovery of zeolites as minerals (Figure 10[14]) - and already one year later this paper appeared in Leipzig (Figure 11[2]). Abraham Gotthelf Kästner, who cared for the translation, was among Leipzig’s establishment. His portrait can still be admired in Leipzig’s historical museum in the Old Town Hall (Figure 12).

Following his very first NMR studies with aqueous solutions, in those days Harry Pfeifer wondered about differences and similarities in the behavior of water in the bulk and in zeolites. He has estimated their mean life times between subsequent jumps between the adsorption sites (most likely cations, see Figure 9)[15] by analyzing the rates of nuclear magnetic relaxation of the water protons. In this way he was able to provide a guess of their diffusivities and wondered whether also a direct measurement of the diffusivity was possible. At this time Dieter Freude had already some experience with NMR diffusion measurements with constant field gradients. Since the application of constant field gradients turned out to be insufficient, it was his recommendation to apply the recently introduced, more powerful NMR technique with pulsed field gradients [16,17] and to make it the topic of my thesis.


Der
Königl. Schwediſchen Akademie
der Wiſſenſchaften
Abhandlungen,
aus der Naturlehre,
Haushaltungskunſt und Mechanik,
auf das Jahr 1756.
Aus dem Schwediſchen überſetzt,
von
Abraham Gotthelf Käſtner,
der Mathematik und Naturlehre Profeſſor zu Göttingen; der daſigen
Kön. Geſ. der Wiſſenſchaften; der Kön. Schwed. und Preußiſchen
Geſellſ. der Wiſſenſ. der Erfurtiſchen Churfürſtl. Geſellſchaft nützlicher
Wiſſenſchaften, des Bononiſchen Inſtituts, der peruſiniſchen Academiae
Auguſtae, der Jenaiſchen lateiniſchen und teutſchen, und der Leipziger
deutſchen Geſellſchaft Mitgliede.

Achtzehnter Band.

Mit Kön. Pohln. und Churf. Sächſ. allergnädigſten Freyheit.

Hamburg und Leipzig,
bey Georg Chriſtian Grund, und Adam Heinrich Holle,
1757.

Figure 11: Publication of Cronstedt's paper one year later in German translation by Gotthelf Kästner in Leipzig.

## 2.2 Focusing on Diffusion in Porous Media

With Wilfried Heink I got a colleague on my side, not only on the photograph in Figure 8, who cared for the electronic developments, in particular for the generation of gradient pulses of such high intensity that the observation of molecular displacements in the interior of the individual zeolite crystallites with diameters as small as 10 µm became possible. The transition from unperturbed intracrystalline diffusion to fast exchange between different crystals has thus become accessible by direct experimental observation and was found to be nicely reproduced by the simple formalism of two-region diffusion [18–20]. In this way, for the very first time, NMR was applied to studying the intractrystalline diffusion in zeolites. Simultaneously it was shown that it was but the rate of mass transfer through the crystal bed, now referred to as long-range diffusion [19], which was attained in previous measurements [17].

I am obliged to Günter Seiffert who continued these developments, using the options of the notably larger magnetic field provided by a superconducting magnet. The "hard currency" needed at this time for acquiring the magnet was earned, by the way, owing to our cooperation with the Shell Research Center in Amsterdam [21]. Our diffusion spectrometer FEGRIS (FEldGRadientenImpulsSpektrometer) 60 (with reference to the proton magnetic resonance frequency in MHz) correspondingly evolved to FEGRIS 300. Further progress and the present level of our measuring device are due to Petrik Galvosas who joined us during his diploma work and graduated with new concepts for the generation of extra-stable and ultra-high field gradient pulses in our group (see Figure 13 and refs. [22,23]). Details of this work may be found in the review[24], jointly authored by Frank Stallmach and Petrik Galvosas.

Figure 12: Leipzig's Old Town Hall

Dealing with water as guest molecules in NaX, the very first NMR measurements of intracrystalline diffusion [15,25] did not notably agitate the zeolite community since this particular system was, so far, not in the focus of their activities. However, the situation changed dramatically when we looked at other guest molecules and zeolites (Figure 14 and ref. [26]). For them, diffusion has been investigated already before, with other techniques. In some cases, the new data were found to deviate from the old ones by as many as five orders of magnitude! This discrepancy and the increasing relevance of zeolites in industry, including the role of diffusion for optimizing their technical exploitation, led to the real flood of novel techniques of diffusion measurement in the years following the application of NMR to diffusion studies in zeolites as illustrated by Figure 15 (ref. [27]).

Figure 13: Petrik Galvosas and his spectrometers developed in the Department of Interface Physics of Leipzig University [22]

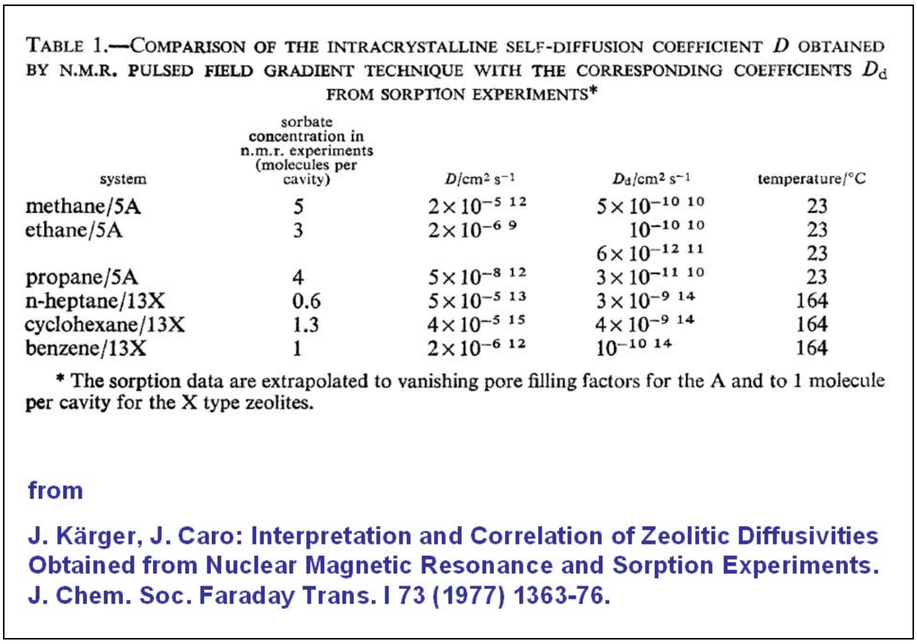


TABLE 1.—COMPARISON OF THE INTRACRYSTALLINE SELF-DIFFUSION COEFFICIENT $D$ OBTAINED BY N.M.R. PULSED FIELD GRADIENT TECHNIQUE WITH THE CORRESPONDING COEFFICIENTS $D_d$ FROM SORPTION EXPERIMENTS*

| system | sorbate concentration in n.m.r. experiments (molecules per cavity) | $D$/cm$^2$ s$^{-1}$ | $D_d$/cm$^2$ s$^{-1}$ | temperature/°C |
|---|---|---|---|---|
| methane/5A | 5 | $2\times10^{-5}$ [12] | $5\times10^{-10}$ [10] | 23 |
| ethane/5A | 3 | $2\times10^{-6}$ [9] | $10^{-10}$ [10] | 23 |
| | | | $6\times10^{-12}$ [11] | 23 |
| propane/5A | 4 | $5\times10^{-8}$ [12] | $3\times10^{-11}$ [10] | 23 |
| n-heptane/13X | 0.6 | $5\times10^{-5}$ [13] | $3\times10^{-9}$ [14] | 164 |
| cyclohexane/13X | 1.3 | $4\times10^{-5}$ [15] | $4\times10^{-9}$ [14] | 164 |
| benzene/13X | 1 | $2\times10^{-6}$ [12] | $10^{-10}$ [14] | 164 |

* The sorption data are extrapolated to vanishing pore filling factors for the A and to 1 molecule per cavity for the X type zeolites.

**from**

**J. Kärger, J. Caro: Interpretation and Correlation of Zeolitic Diffusivities Obtained from Nuclear Magnetic Resonance and Sorption Experiments. J. Chem. Soc. Faraday Trans. I 73 (1977) 1363-76.**

Figure 14: Surprisingly large values of intracrystalline diffusivities in zeolites: revealing a discrepancy of five orders of magnitude by PFG NMR [26]

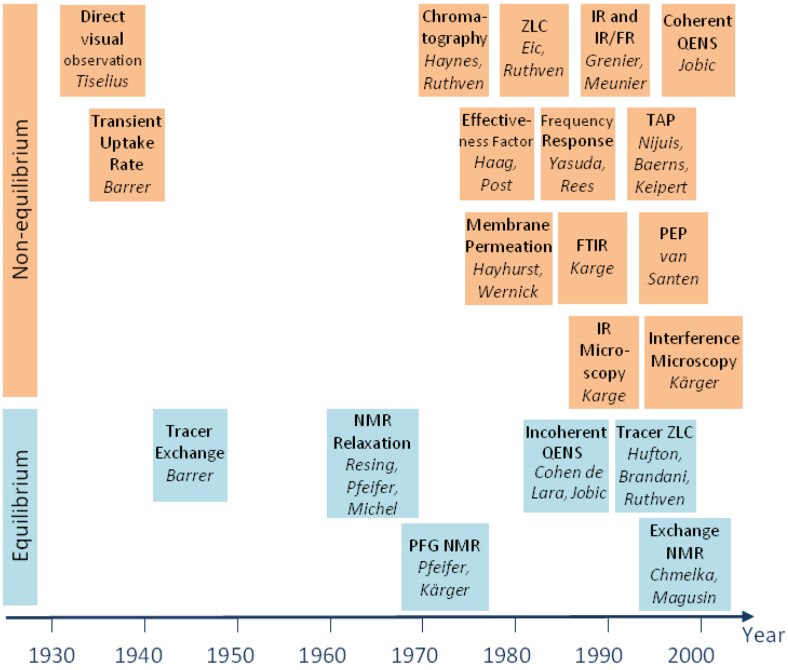
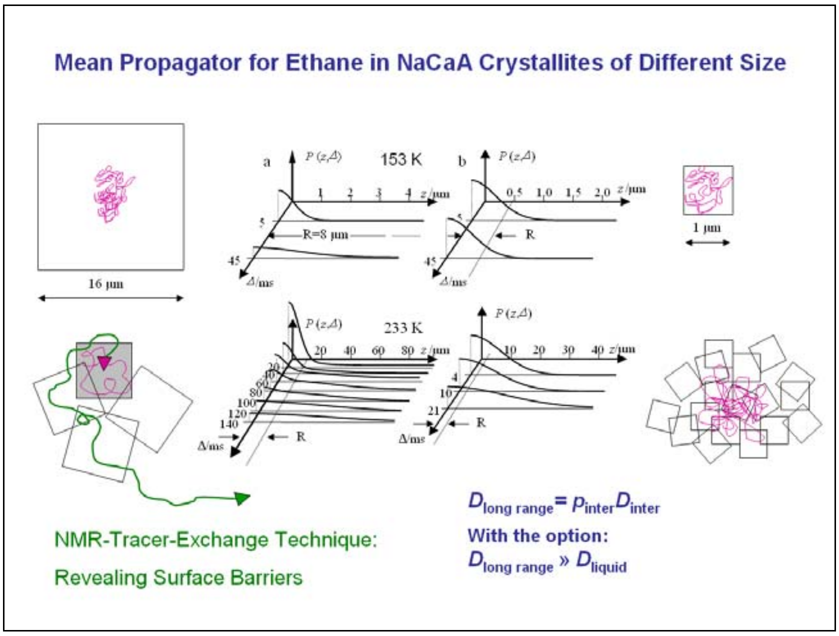


Figure 15: Introducing PFG NMR into zeolite science and technology gave rise to a real flood of new techniques of diffusion measurement [27]

In this situation we benefitted a lot from the versatility of the Pulsed Field Gradient (PFG – also referred to as Pulsed Gradient Spin Echo, PGSE) NMR techniques and the related options to demonstrate their self-consistency. The potentials of PFG NMR become particularly pronounced in the propagator presentation, i.e. by plotting the probability of molecular displacements as a function of the observation time (Figure 16 and ref. [28]). Due to symmetry reasons, it is sufficient to present only one half of the propagators. The distributions shown in Figure 16 refer to the diffusion paths of ethane in zeolites of type NaCaA of big and small size. Depending on the chosen parameters, for one and the same system a large spectrum of information is provided. This includes the true intracrystalline diffusivities (top left), the crystal size (top right, illustrating the fundamentals of "dynamic imaging" [29]), the rate of intercrystalline exchange (bottom left) and the long-range diffusivity (bottom right).

Long-range diffusion may be regarded as a limiting case in the description of diffusion in complex systems by the two-region model [18–20] where, under the conditions of fast exchange, the contribution of intracrystalline diffusion becomes negligibly small, yielding $D_{\text{long-range}}=p_{\text{inter}}D_{\text{inter}}$ [19]. Under the conditions of gas-phase adsorption, the relative amount $p_{\text{inter}}$ of molecules in the intercrystalline is rather small. However, being subject to Knudsen or gas diffusion, the diffusivity $D_{\text{inter}}$ in the intercrystalline space may attain values high enough so that long-range diffusion may exceed even the guest diffusivities in the liquid phase [30].

In our efforts to provide independent evidence in favor of "our" NMR data on zeolitic diffusion it was of special relevance that some of the information provided by our technique could also be obtained and confirmed by well-established independent techniques and procedures including, in particular, the estimate of long-range diffusivities and the determination of the crystal size by conventional microscopy [9,10,31]. It is interesting to note that, in addition to considering the limiting case of completely restricted diffusion, PFG NMR provides two further, independent options for determining the crystal size (Figure 17 and ref. [32]). They are related to the Mitra formalism [33], i.e. to the short-time behavior of the effective diffusivity under restriction by pores. In fact, intracrystalline diffusion in zeolites may nicely comply with the two limiting cases of pores with reflecting or with absorbing walls. They correspond, respectively, to the limiting cases of long-range diffusivities much smaller than the intracrystalline diffusivities (where the molecules remain in the interior of essentially one crystal – with the same effect also brought about by, e.g., extremely large transport resistances on the crystal surface) and much larger than the intracrystalline diffusivities where the molecules, as soon as they have left their crystallites, cover such large distances that they do not contribute anymore to the signal, just as if they would have been swallowed. By applying appropriate guest mixtures, e.g. fluoromethane and n-hexane, it is possible to realize both limiting cases with one and the same sample. In the chosen example, PFG NMR can thus be applied to determine the crystal radii by three different, mutually independent techniques, and is found (see Figure 17) to yield reasonable agreement.



**Mean Propagator for Ethane in NaCaA Crystallites of Different Size**

$D_{\text{long range}} = p_{\text{inter}} D_{\text{inter}}$

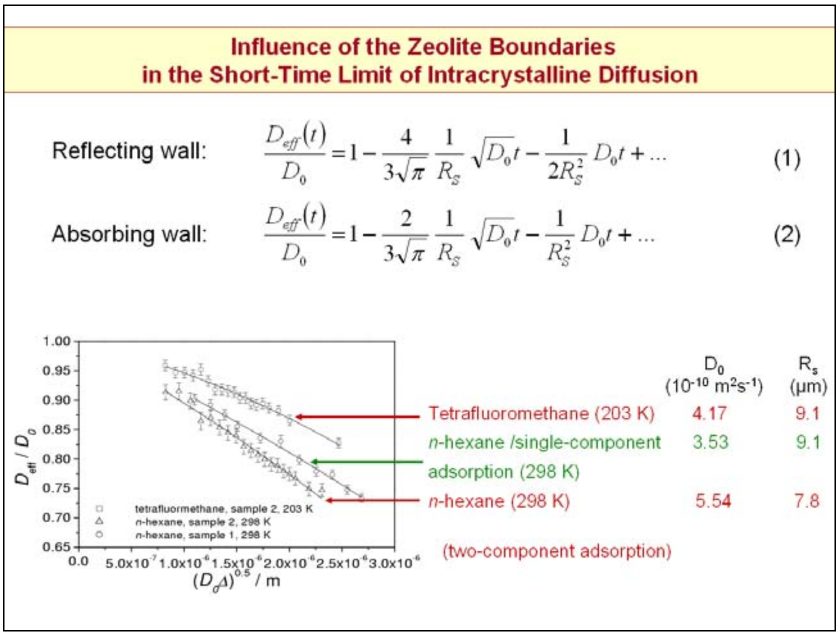
With the option:

$D_{\text{long range}} \gg D_{\text{liquid}}$

NMR-Tracer-Exchange Technique:

Revealing Surface Barriers

Figure 16: Propagator representation of mass transfer in a bed of zeolite crystallites for visualizing the wealth of information provided by PFG NMR [28]



**Influence of the Zeolite Boundaries in the Short-Time Limit of Intracrystalline Diffusion**

Reflecting wall:

$$\frac{D_{eff}(t)}{D_0} = 1 - \frac{4}{3\sqrt{\pi}} \frac{1}{R_S} \sqrt{D_0 t} - \frac{1}{2R_S^2} D_0 t + \ldots \quad (1)$$

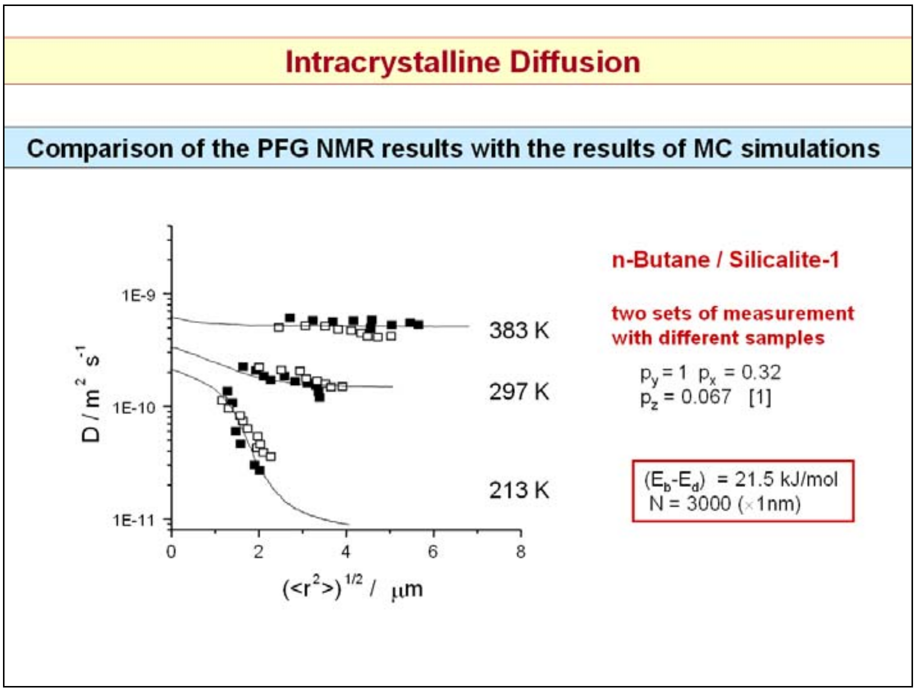
Absorbing wall:

$$\frac{D_{eff}(t)}{D_0} = 1 - \frac{2}{3\sqrt{\pi}} \frac{1}{R_S} \sqrt{D_0 t} - \frac{1}{R_S^2} D_0 t + \ldots \quad (2)$$

| | $D_0$ ($10^{-10}$ m$^2$s$^{-1}$) | $R_s$ (µm) |
|---|---|---|
| Tetrafluoromethane (203 K) | 4.17 | 9.1 |
| *n*-hexane /single-component adsorption (298 K) | 3.53 | 9.1 |
| *n*-hexane (298 K) (two-component adsorption) | 5.54 | 7.8 |

Figure 17: Analyzing the influence of confinement on intracrystalline zeolitic diffusion as a means for determining crystal sizes [32]

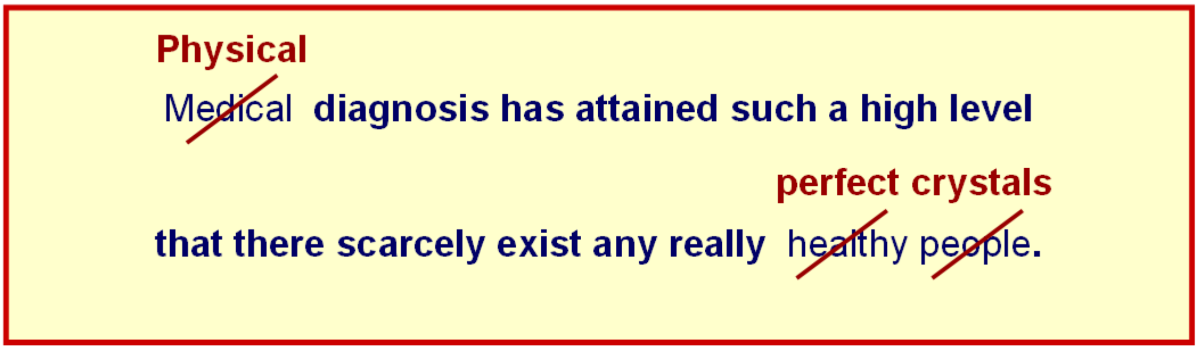
In Figure 18 the intracrystalline diffusivities in a particular zeolitic host-guest system as revealed by PFG NMR are, most remarkably, found to decrease with increasing diffusion path lengths, though these displacements are negligibly small in comparison with the crystal size. This finding unambiguously indicates the existence of intracrystalline transport resistances ("barriers"), caused e.g. by stacking faults, which act in addition to the diffusional resistance of the genuine pore system [34]. It is interesting to note that by already very simple assumptions – namely for barriers equally spaced at a distance of 3 µm with activation energies exceeding those of intracrystalline diffusion by about 20 kJ/mol – the experimental data are nicely approached by simulations [35]. Diffusion measurements have thus helped to trace, and to finally directly record by high-resolution electron microscopy [36], structural details which so far have been unknown. Statements concerning the negative effect of advanced medical diagnosis on our state of health which one may occasionally find on posters in surgeries (Figure 19) are thus seen, after but a few replacements, to be also true for such tiny objects like zeolite crystallites.



Intracrystalline Diffusion

Comparison of the PFG NMR results with the results of MC simulations

Figure 18: Revealing intracrystalline transport resistances in zeolites by PFG NMR measurements with variable diffusion path lengths [34]



Physical

~~Medical~~ diagnosis has attained such a high level

perfect crystals

that there scarcely exist any really ~~healthy people~~.

Figure 19: A queer view on consequences of progress

The relation between intracrystalline and long-range diffusion as appearing in the propagator representations shown in Figure 16 determine the pattern of the evolution of the concentration profiles in beds of zeolites. Following the pioneering work by Paul Lauterbur [37] and Peter Mansfield [38] (Figure 20), NMR imaging has become the technique of choice for recording evolving concentration profiles [13,39]. Figure 21 illustrates the attempts of our group for exploiting these new options in a rather early stage of their development [40] for exploring guest dynamics in beds of zeolites. The cartoons, accompanying the "zeugmatograms" [37] , i.e. the molecular distributions as provided by the NMR spectra of the guest molecules under the influence of a field gradient applied in the direction of the tube axis, illustrate the two limiting situations observable under such conditions: In beds of large crystals (top) molecular uptake is found to occur essentially simultaneously over the whole bed of crystals while small crystals (bottom) absorb essentially instantaneously the whole amount of guest molecules introduced into the sample (bottom left). Only over subsequent, much larger time spans (bottom right), the guest molecules are found to be distributed over the whole bed of crystals.

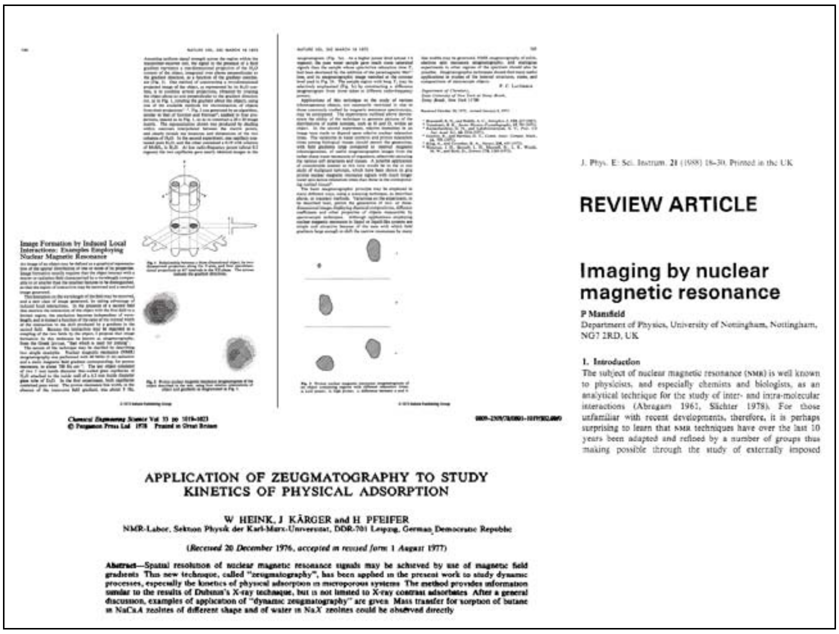


Image Formation by Induced Local Interactions: Examples Employing Nuclear Magnetic Resonance

J. Phys. E: Sci. Instrum. 21 (1988) 18-30. Printed in the UK

REVIEW ARTICLE

Imaging by nuclear magnetic resonance

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1. Introduction
The subject of nuclear magnetic resonance (NMR) is well known to physicists, and especially chemists and biologists, as an analytical technique for the study of inter- and intra-molecular interactions (Abragam 1961, Slichter 1978). For those unfamiliar with recent developments, therefore, it is perhaps surprising to learn that NMR techniques have over the last 10 years been adapted and refined by a number of groups thus making possible through the study of externally imposed

Chemical Engineering Science Vol 33 pp 1019-1023
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APPLICATION OF ZEUGMATOGRAPHY TO STUDY
KINETICS OF PHYSICAL ADSORPTION

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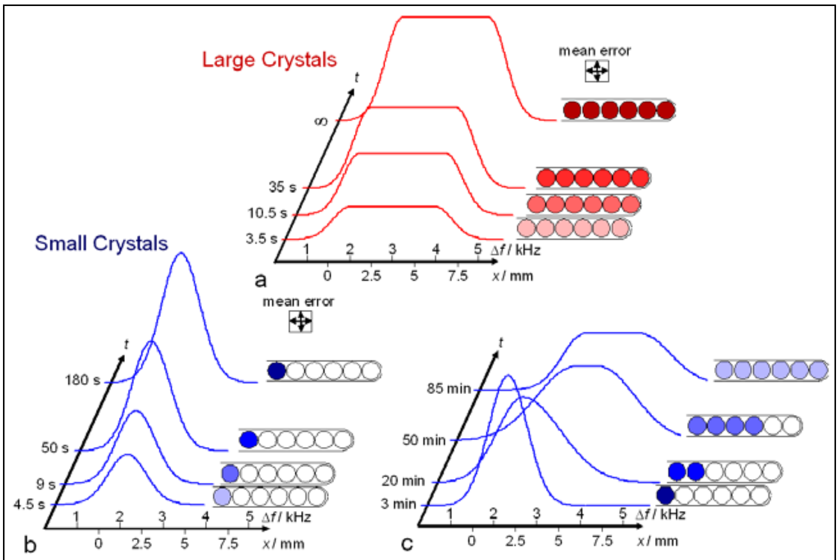
(*Received 20 December 1976, accepted in revised form 1 August 1977*)

**Abstract**—Spatial resolution of nuclear magnetic resonance signals may be achieved by use of magnetic field gradients This new technique, called "zeugmatography", has been applied in the present work to study dynamic processes, especially the kinetics of physical adsorption in microporous systems The method provides information similar to the results of Dubinin's X-ray technique, but is not limited to X-ray contrast adsorbates After a general discussion, examples of application of "dynamic zeugmatography" are given Mass transfer for sorption of butane in NaCaA zeolites of different shape and of water in NaX zeolites could be observed directly

Figure 20: Reports about the options of imaging by NMR



**Evolution of the distribution of n-butane in a bed of crystals of zeolite NaCaA with crystal diameters of about 40 µm (a) and 4 µm (b,c) in an NMR sample tube in axial (*x*-) direction**

Figure 21: Early imaging experiments in Leipzig with beds of zeolite crystallites [40]

Meanwhile, the dramatic progress in MR imaging allows spatial resolutions in the range of micrometers [13,39]. The inevitable accumulation times, however, still exclude the possibility to record intracrystalline concentration profiles. With the introduction of novel imaging techniques based on monitoring the intracrystalline concentration profiles by IR and interference microscopy [41] we now dispose of an alternative means which has proved to provide unprecedented information on both the intracrystalline diffusivities [42] and the permeability through the external crystal surface [43].

Figure 22: Dieter Freude (right in the figure), together with Edith Flanigen, first Breck Awardee, and David Vaughan, President of the International Zeolite Association, during the Award Ceremony in Tokyo, 1986, when, on the occasion of the 7th International Zeolite Conference, the application of NMR for studying diffusion and acidity in Leipzig was recognized with the Breck Award

The engagement of Harry Pfeifer and his group in the application of NMR to zeolite research was recognized by the Breck Award of the International Zeolite Association in Tokyo 1986, delivered by the International Zeolite Association (http://www.iza-online.org/) during its 7th congress in Tokyo 1986. The award was designated to the application of PFG NMR to diffusion studies and of MAS NMR for quantifying acidity. On Figure 22 one may recognize Dieter Freude on the right, together with Edith Flanigen who received the first Breck Award and David Vaughan, the President of the International Zeolite Association. The decision of the award committee was quite fresh so that the names of the awardees, Harry Pfeifer, Dieter Freude and Jörg Kärger, together with Martin Bülow from the Academy of Sciences in Berlin, did not yet appear on the award plaque. I refer to this event with particular pleasure since now, by combining PFG and MAS, NMR diffusion measurements have become even more powerful (see Figure 23 [44,45]).

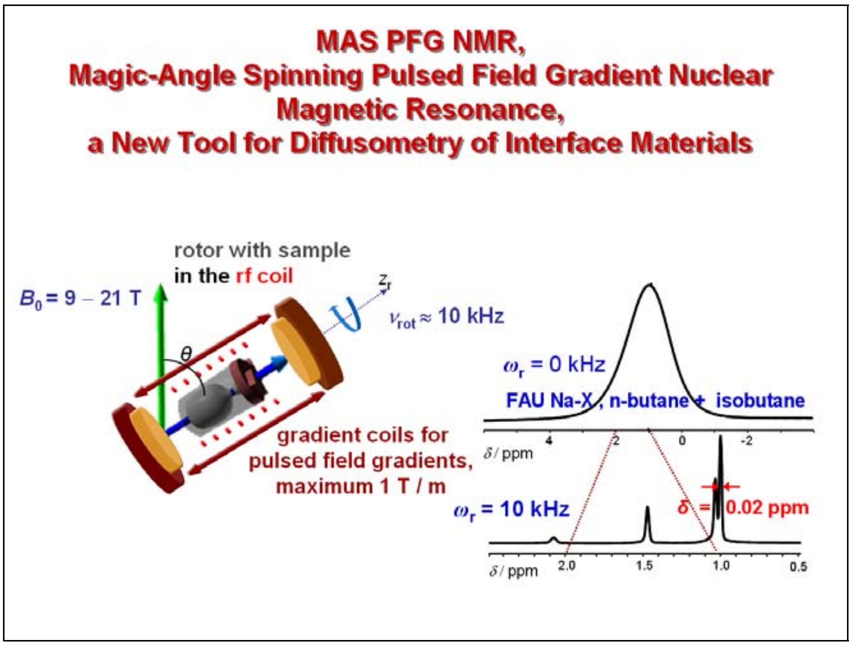
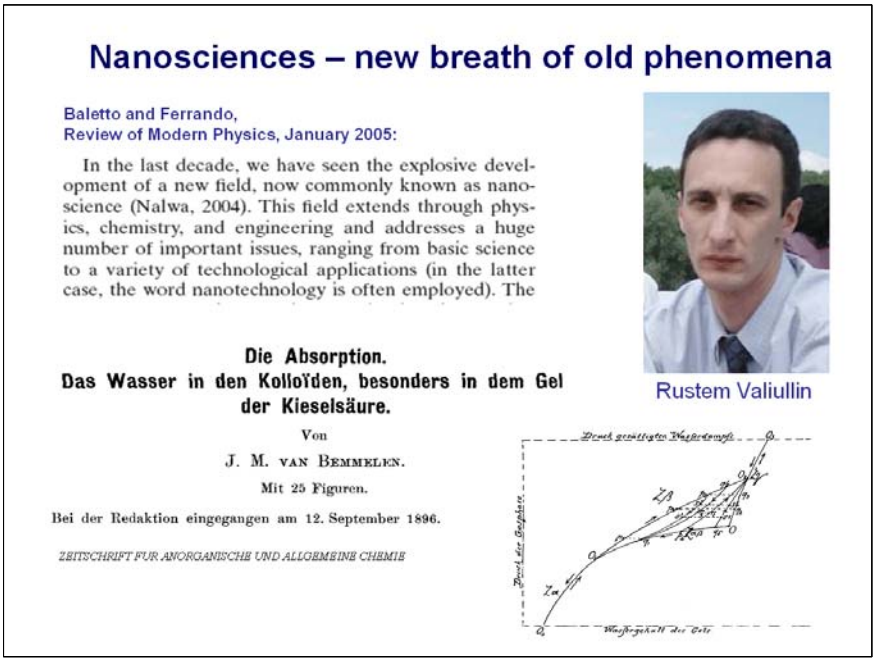

MAS PFG NMR,
Magic-Angle Spinning Pulsed Field Gradient Nuclear Magnetic Resonance,
a New Tool for Diffusometry of Interface Materials

Figure 23: New prospects for NMR diffusion measurements by combining magic angle spinning and pulsed field gradients [44], i.e. those techniques for which, at this time still separated from each other, Leipzig's researchers received the Breck Award of the International Zeolite Association.

## 3. Sorption Hysteresis: Impact of the Past

I wanted to conclude the presentation by reporting more comprehensively about another of our more recent activities. The story starts with Rustem Valiullin (Figure 24) who joined us as a Humboldt awardee and directed our attention to an old phenomenon which, during more than a century, has nothing lost of its fascination, namely the behavior of guest molecules in mesopores and, in particular, their memory on the past. During the 8th Bologna Conference on Magnetic Resonance in Porous Media in 2006 his work was honored with the Giulio Cesare Borgia Prize. It is “presented to the emerging scientist who, based on a presentation to the community at the conference, shows greatest promise for future scientific leadership”.



Nanosciences – new breath of old phenomena

Baletto and Ferrando,
Review of Modern Physics, January 2005:

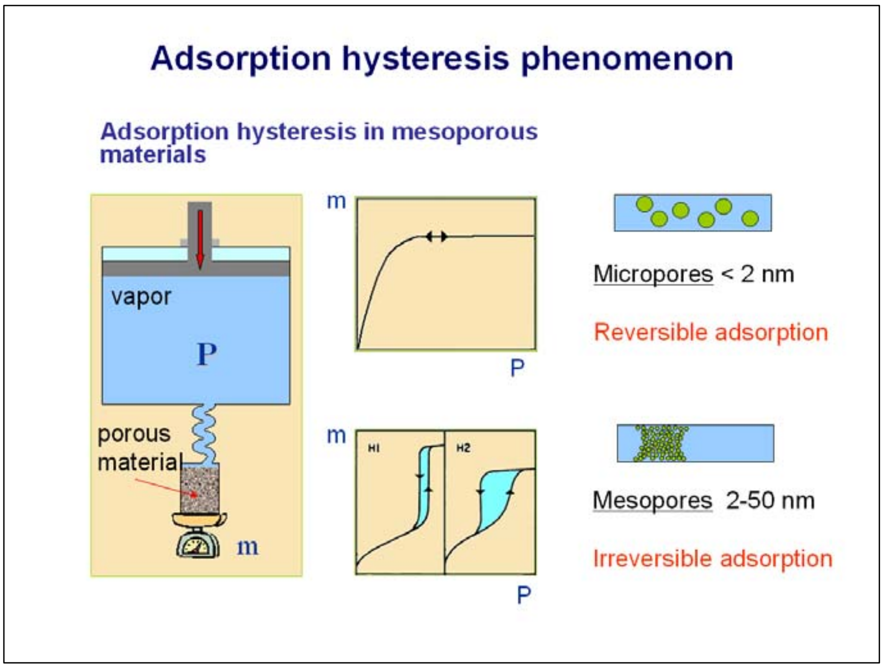
In the last decade, we have seen the explosive development of a new field, now commonly known as nanoscience (Nalwa, 2004). This field extends through physics, chemistry, and engineering and addresses a huge number of important issues, ranging from basic science to a variety of technological applications (in the latter case, the word nanotechnology is often employed). The

Die Absorption.
Das Wasser in den Kolloïden, besonders in dem Gel der Kieselsäure.
Von
J. M. van Bemmelen.
Mit 25 Figuren.
Bei der Redaktion eingegangen am 12. September 1896.

ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE

Rustem Valiullin

Figure 24: Sorption hysteresis, a topic which intrigues scientists since more than a century, was among the new subjects for which Rustem Valiullin, joining us as a Humboldt Awardee, stimulated our interest



Adsorption hysteresis phenomenon

Adsorption hysteresis in mesoporous materials

Micropores < 2 nm

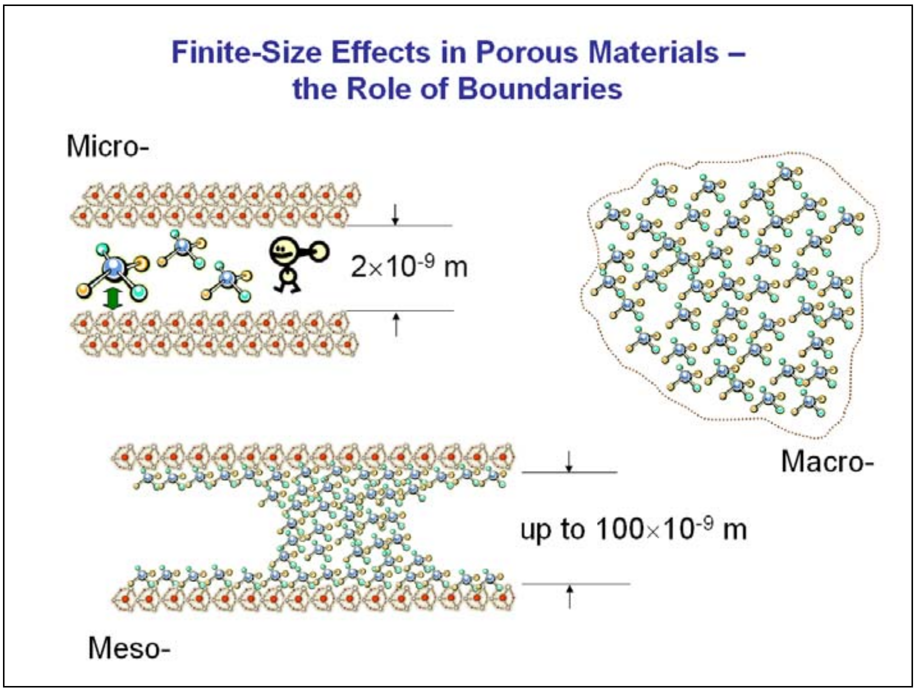
Reversible adsorption

Mesopores 2-50 nm

Irreversible adsorption

Figure 25: The different behavior of micro- and mesopores during adsorption

If one monitors molecular adsorption and desorption, e.g. by a balance (left of Figure 25), one observes in micropores (top right) perfect reversibility, while in mesopores (bottom right) for one and the same pressure after increasing pressures (i. e. during adsorption) the amount adsorbed is notably below the amount adsorbed during desorption. This phenomenon, i.e. the influence of the past on the actual state, is referred to as hysteresis. Figure 26 illustrates the difference in the situations in micro- and mesopores in a cartoon-like manner. Molecules in micropores are in close interaction with the walls so that any significant influence of their interaction (which would dominate in the bulk phase and, correspondingly, in sufficiently large (i.e. “macro-“) pores) is suppressed. We thus do have a situation similar to the Oktoberfest in Munich (Figure 27) where the people are fixed to the Weißwurst (Bavarian veal sausage) and the beer on the table in front of them. The mesopores, however, offer the option of interaction of the guest molecules (or the guests – Figure 28) with *both* each other and the walls (or food and drinks on the tables).



Finite-Size Effects in Porous Materials –
the Role of Boundaries

Figure 26: The different situations for molecular interaction due to different pore sizes

Figure 27: Visualizing the situation in micropores by the Oktoberfest in Munich

It is illustrated by Figure 29 that NMR offers the unique option of recording both the relative amount of molecules (by the signal intensity) and their mobility (by a simple pulsed field gradient sequence). In this way it is possible to follow the molecular uptake after a pressure step and, simultaneously, to determine the diffusivity of the molecules. Thus, below the range of hysteresis (e.g. for steps from about 0.32 to 0.35 in relative pressure, Figure 30 top left) the amounts adsorbed on the adsorption and desorption branches do still coincide) the recorded uptake can be found to follow the dependence determined by solving the corresponding diffusion equation (bottom left [9,10]) with the diffusivity simultaneously determined by PFG NMR (top right, [46]). Within the range of hysteresis, however, molecular uptake takes much longer than expected from the molecular mobilities. It is in fact found that the equilibration rate drops to zero!

Figure 28: Mesopore-like situation during a coffee break

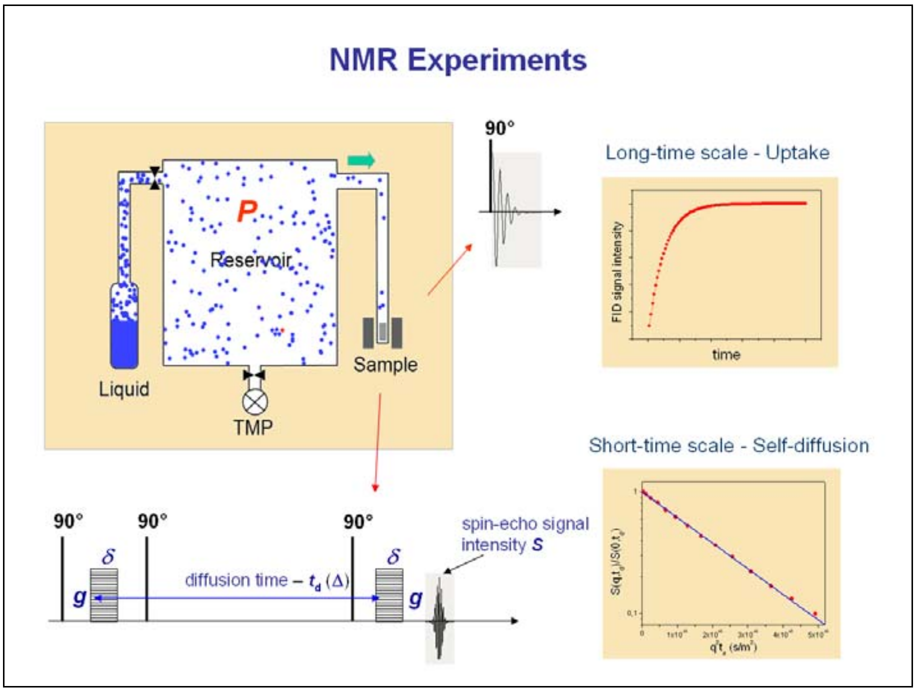
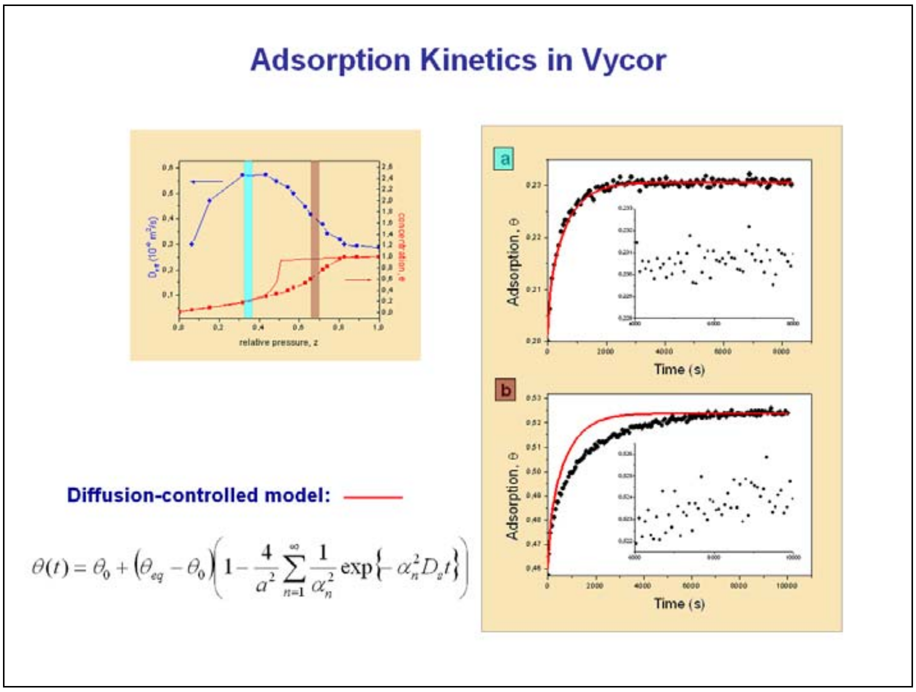


Figure 29: During adsorption (top left) NMR allows to simultaneously measure the amount of uptake (by the signal intensity, top center and right) and the molecular mobility (by PFG NMR, bottom)

This leads to a very peculiar situation which is, in some more detail, illustrated by Figure 31. On top left we recognize the well-known pattern of sorption hysteresis, i.e. different amounts adsorbed for a given external pressure, depending on whether the given pressure has been attained from lower values, i.e. on the adsorption branch, or from higher values, i.e. by desorption. One may even switch from adsorption to desorption before saturation or from desorption to adsorption before merging of the adsorption and desorption branches. In this way one generates the so-called scanning adsorption or desorption curves which appear within the hysteresis loop. Bottom left shows the simultaneously measured diffusivities. Combination of the two representations on the right allows plotting of the diffusivities as a function of loading [47]. The diffusivities for one and the same amount of guest molecules are thus found to attain notably different values. Taking the diffusivities as a probe of the state of the system, different ways of introducing the molecules into the system, i.e. different sample histories, are thus seen to lead to notably different states. It is interesting to note that these states remain stable and well-distinguished between each other over days, irrespective of the rapid movement of each individual molecule over the whole sample: The balance in the interaction of the molecules with each other and with the wall as determined by the given particle distribution stabilizes the given state. In the language of thermodynamics, the interaction is said to keep the system in local minima of the free energy and prevents its approaching the absolute minimum, i.e. the final stage of equilibration.



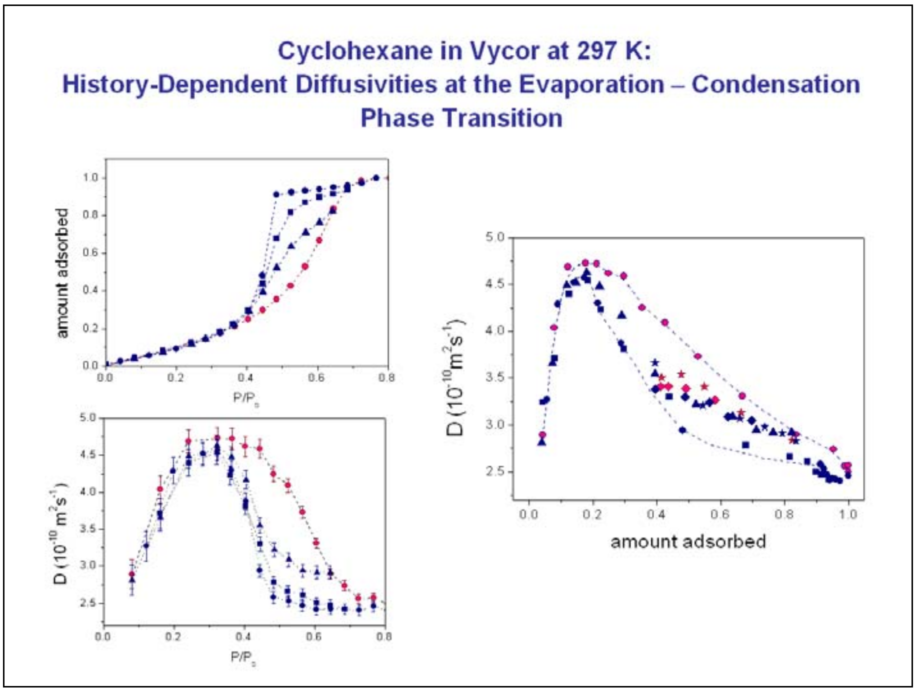
Adsorption Kinetics in Vycor

Diffusion-controlled model: ——

$$\theta(t) = \theta_0 + \left(\theta_{eq} - \theta_0\right)\left(1 - \frac{4}{a^2}\sum_{n=1}^{\infty}\frac{1}{\alpha_n^2}\exp\left\{-\alpha_n^2 D_z t\right\}\right)$$

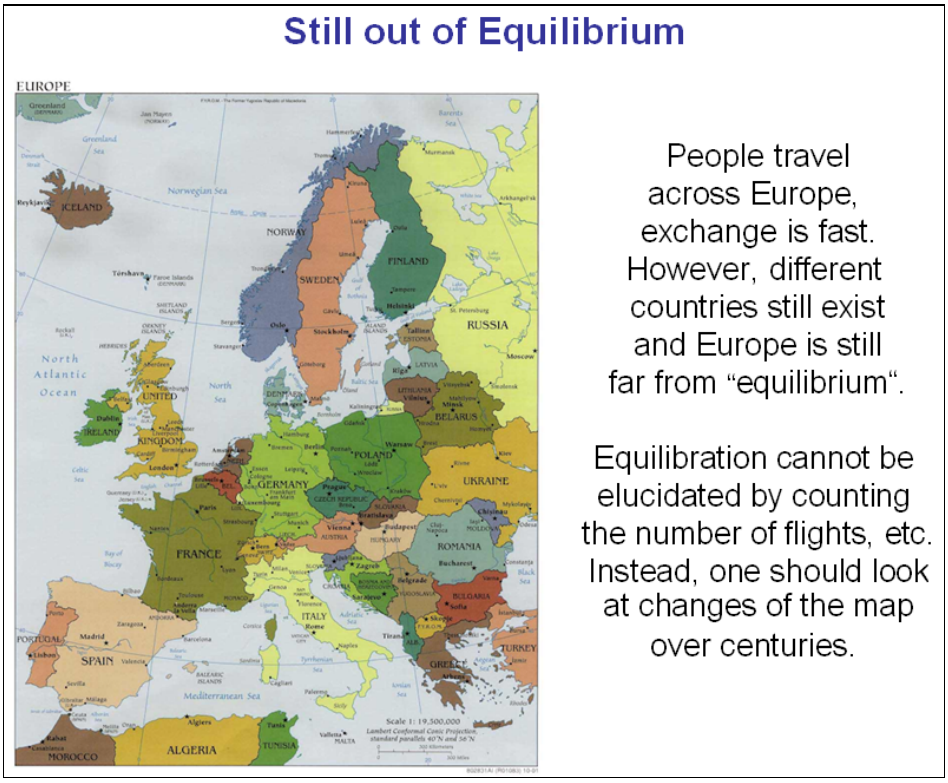
Figure 30: The rate of molecular uptake following a pressure strep is found to follow the analytical expression for diffusion limitation (bottom left) before onset of hysteresis (relative pressure enhanced from about 0.32 to 0.35, top right) while it is dramatically slowed down within the pressure range of hysteresis (Bottom right) [46]

This situation has some analogue in our political world (Figure 32). We are happy that today there is essentially no restriction in our travelling activities. However, irrespective of the thus enable exchange of the people between different countries, most fortunately the differences between the different countries continue to exist – based on the "local interactions" which now include items like the culture and joint history of the people.



Cyclohexane in Vycor at 297 K:
History-Dependent Diffusivities at the Evaporation – Condensation Phase Transition

Figure 31: Choosing different ways of ad- and desorption (left), for one and the same final loading the measured diffusivity may assume an essentially unlimitedly large number of different values over essentially infinitely large time spans, irrespective of the fast movement of the moelcules through the whole sample(right) [47]



Still out of Equilibrium

People travel
across Europe,
exchange is fast.
However, different
countries still exist
and Europe is still
far from “equilibrium“.

Equilibration cannot be
elucidated by counting
the number of flights, etc.
Instead, one should look
at changes of the map
over centuries.

Figure 32: Analogy to the situation expressed on the right of Figure 31 in our political world: there is a multitude of different countries rather than uniformity, irrespective of a vivid traveller exchange.

## 4. Conclusion and Acknowledgement

Starting with Leipzig's history, in particular with the history of its university and the physics institute, I finished my story with exemplifying the importance which the "history" may have on the tiny world of a mesoporous host-guest system. With great pleasure I have spoken about the part played by NMR and NMR diffusion measurement in both cases. I was lucky to have found magnificent mentors, dear friends and excellent fellow-combatants on my diffusion path. Some of them I have explicitly mentioned already. Many more are seen on the photographs on Figures 8 and 33. My acknowledgement would be incomplete, however, if I would not refer to many more dear colleagues and friends from outside our group. It was my great pleasure to see a great deal of them on the occasion of this 10th Bologna Conference on "Magnetic Resonance in Porous Media" 2010 here in Leipzig. Last but not least I have to thank my wife Birge for all her dear understanding and help.

Figure 33: The colleagues of the Department of Interface Physics in October 2008.

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