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History-Dependent Molecular Dynamics in Nanoporous Host Matrices*

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*dedicated to Professor Günter Vojta on the occasion of his 80th birthday in October 2008

Abstract

Ensembles of molecules confined to pore spaces with diameters of the order of a couple of molecular diameters reveal features which may notably deviate from their behaviour both in the bulk phase and under dominating host-guest interaction. We are going to demonstrate that under identical external conditions (temperature, pressure), different ensemble "histories" may give rise to dramatic differences in the states of these ensembles. PFG NMR diffusion measurements are introduced as a most sensitive tool for probing these differences.

1. Introduction

Diffusion, i.e. the irregular movement of the elementary constituents of matter, notably of atoms and molecules, is among the most fundamental and omnipresent phenomena in nature [1, 2]. It maintains the functionality of living cells [3, 4] and forms the basis of numerous technological processes [5]. This is in particular true with nanoporous materials. They may be visualized as sponges with holes of molecular dimensions [6, 7] and are key to a plethora of novel, environmentally friendly technologies of acquiring value-added products by mass separation and heterogeneous catalysis [8, 9]. Simultaneously, the properties of molecular ensembles in nanoporous host guest systems have become a hot topic of fundamental research [10-13].

This contribution deals with the dynamics of guest molecules in the so-called mesoporous materials. Following IUPAC terminology, the internal width of mesopores is between 2 and 50 nm [14]. Ensembles of guest molecules with typical dimensions of less than

1 nm in such host systems may be considered as "mesoscopic" systems. Being simultaneously subject to the guest-guest and guest-host interaction, molecular ensembles under mesoporous confinement exhibit properties which notably deviate from the bulk phase (with intermolecular interaction only), as well as from guest phases in "microporous" hosts (with pore widths < 2 nm leading to a dominating guest-host interaction). As a most prominent example, this special situation gives rise to the occurrence of "sorption hysteresis": Starting from medium loadings, in addition to guest pressure in the surrounding atmosphere and temperature, the total amount of guest molecules is found to depend on the history, namely on whether the actual pressure has been approached from higher values (i.e. on the "desorption branch") or from lower values (on the "adsorption branch") [15-17]. The occurrence of history-dependent states in mesoporous host-guest systems may be rationalized by the special topology of the Gibbs Free Energy landscape of such systems: Concurrence of guest-guest and guest-host interactions gives rise to various local minima in Free Energy which correspond to quite different molecular arrangements. Fluctuation-generated transitions from one state to another, i.e. from one local minimum to an adjacent one, may happen to require essentially infinitely long time spans so that, with one and the same set of external parameters (temperature and pressure), quite different (quasi-)stable states may be generated.

Phenomena of this type may occur at both melting-freezing [18] and evaporation-condensation transitions in the guest phase. Though being a subject of intense research since more than a century [19], the quantification of these phenomena and their correlation with the underlying mechanisms remained a topic of controversial discussions [15, 20-25]. With the recent application of the pulsed field gradient (PFG) technique of nuclear magnetic resonance (NMR) [26-28] to diffusion measurements in such systems [29-31], the spectrum of experimental techniques has been accomplished by a powerful tool. By recording the probability distribution of molecular displacements (the so-called propagator [32, 33]), PFG NMR provides unprecedented insight into the microdynamics of molecular migration and re-distribution, occurring in parallel with the phenomena of phase transformation which, so far, have been mainly accessible by only macroscopic observation. After a short introduction to the experimental techniques, we are going to illustrate the potentials of this novel type of insight with examples of diffusion measurement under the conditions of evaporation-condensation transitions.

2. Experimental: Diffusion Measurement by NMR

The versatility of NMR turns out to be of particular benefit for the exploration of molecular adsorption and diffusion in nanoporous materials. Since the NMR signal intensity is directly proportional to the number of resonating nuclei and, hence, of the molecules under study, NMR is able to measure the absolute number of guest molecules within a sample at a given instant of time. A second type of information is provided by the nuclear magnetic relaxation times, i.e. by the time constants by which the different types of nuclear magnetization attain their equilibrium values [26-28, 34]. Since these time constants notably differ between the frozen and liquid states, in addition to the absolute numbers of the guest molecules, NMR spectroscopy provides direct evidence of their fractions in the liquid and frozen states [18, 35-37].

The particular strength of NMR in the exploration of complex systems is related to its sensitivity towards diffusion phenomena. In fact, the primary quantity of PFG NMR measurements, namely the attenuation of the NMR signal intensity under the influence of field gradient pulses, may be shown to be the Fourier transform:

$$\Psi(\mathbf{q},t) = \iint p(\mathbf{r}_0) P(\mathbf{r}_0 + \mathbf{r}, \mathbf{r}_0; t) \mathrm{d}\mathbf{r}_0 \cos(\mathbf{q}\,\mathbf{r}) \mathrm{d}\mathbf{r}\,, \tag{1}$$

of the mean propagator, $\int p(\mathbf{r}_0) P(\mathbf{r}_0 + \mathbf{r}, \mathbf{r}_0; t) \mathrm{d}\mathbf{r}_0$, i.e. of the average of the local propagator (namely, the probability distribution of molecular displacements $\mathbf{r}$ during t) over all starting positions $\mathbf{r}_0$ within the sample [32, 33]. Here, t is the separation between a pair of field gradient pulses and represents the observation time of the PFG NMR experiment. It may be varied between, typically, 1 ms and a couple of seconds. The parameter $\mathbf{q} \equiv \delta\gamma\mathbf{g}$ is a measure of the intensity of the field gradient pulses, with γ as the gyromagnetic ratio ($= 2.67\times10^8$ $\mathrm{T}^{-1}\mathrm{s}^{-1}$ for ^{1}H as considered in our studies) and δ and g denoting the width and the amplitude of the gradient pulses.

In the case of normal diffusion, the "local" propagator $P(\mathbf{r}_0 + \mathbf{r}, \mathbf{r}_0; t)$ is a simple Gaussian

$$P(\mathbf{r},t) = (4\pi D t)^{-3/2} \exp\left(-\frac{\mathbf{r}^2}{4Dt}\right) \tag{2}$$

with the self-diffusivity D and independent of the starting point $\mathbf{r}_0$. Thus the PFG NMR signal attenuation simply becomes

$$\Psi(\mathbf{q},t) = \int P(\mathbf{r},t)\cos(\mathbf{qr})\mathrm{d}\mathbf{r} = \exp\left(-q^2 Dt\right). \tag{3}$$

Most importantly, if the usual semi-logarithmic plot of the PFG NMR spin-echo attenuation versus the squared gradient intensity q^2 yields a straight line, molecular dynamics with respect to the time and space scales covered in the experiments is thus easily found to be governed by a Gaussian, i.e. to follow normal diffusion, with the diffusivity D given by the slope of this plot.

In Leipzig, the development of PFG NMR as a powerful technique for the exploration of diffusion phenomena in complex systems was initiated by Professor Harry Pfeifer [28, 38, 39]. Starting with the investigation of guest diffusion in crystalline molecular sieves (zeolites) [40-42], the versatility of PFG NMR has soon led to a dramatic expansion of the field of investigations, including diffusion measurements in disordered host materials [43, 44] and biological systems [45-48]. During this time, the Leipzig PFG NMR group notably benefited from the fruitful contact with Professor Günter Vojta. It was due to his influence and advice, that PFG NMR was now also most successfully applied to trace indications of anomalous transport, i.e. to look for systems with propagators deviating from a Gaussian as given by eq. (2) [49-52].

The PFG NMR diffusion measurements of this study were performed with the home-built high-intensity pulsed field gradient NMR diffusometer FEGRIS 400 [53, 54] by means of the "stimulated echo" ($\pi/2$ - τ_1 - $\pi/2$ - τ_2 - $\pi/2$ - τ_1 - spin echo) pulse sequence [26-28] at Leipzig University. The actual key parameters of the diffusometer, namely field gradient amplitudes of up to 60 Tm^{-1} and rise and fall times of less than 100 µs, continue to represent top values in the international comparison.

3. Results and Discussion

3.1 A Dramatic Slowing Down of Molecular Uptake

Fig. 1 illustrates the new options offered by PFG NMR for the exploration of molecular dynamics in nanoporous materials [31]. The lower part of Fig. 1a displays the so-called adsorption isotherm. It represents the (relative) amount of guest molecules as a function of the external pressure. Starting from medium concentrations, for one and the same pressure, substantial differences between the amounts adsorbed during adsorption (lower branch) and desorption (upper branch) are observed. This most pronounced effect of "history" on the actual state of the host-guest system is typical of the Vycor glasses under study and made them the "guinea pig" in the research of sorption hysteresis [55-58]. Simultaneously with the amount adsorbed, PFG NMR is also able to measure the self-diffusivities of the guest molecules, which are as well displayed in fig. 1a. There was a strict exponential dependence of the PFG NMR signal intensity $\Psi(\mathbf{q},t)$ which, following eq. (3), indicates normal diffusion. Therefore, over the accessible space and time scales, molecular dynamics is adequately reflected by the self-diffusivity as a sole parameter. In addition to Fig. 1a, where the amounts adsorbed were shown under (quasi-) equilibrium conditions, Figs. 1b and 1c provide two characteristic examples of the whole time dependence of molecular uptake.

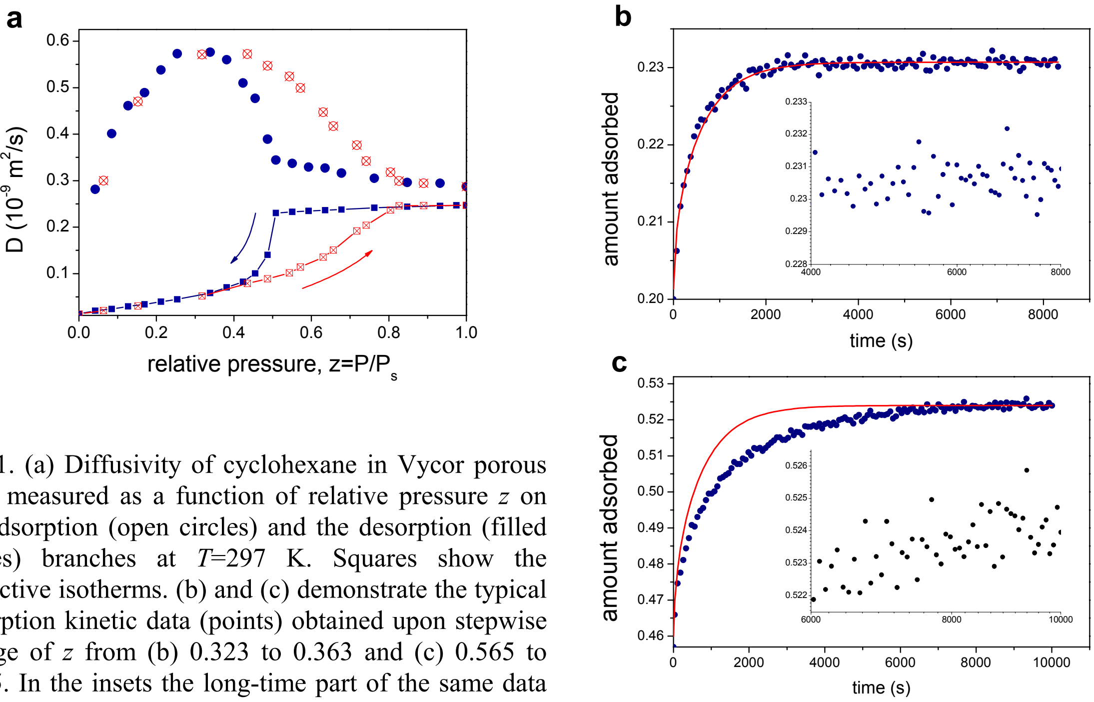

Fig. 1. (a) Diffusivity of cyclohexane in Vycor porous glass measured as a function of relative pressure z on the adsorption (open circles) and the desorption (filled circles) branches at T=297 K. Squares show the respective isotherms. (b) and (c) demonstrate the typical adsorption kinetic data (points) obtained upon stepwise change of z from (b) 0.323 to 0.363 and (c) 0.565 to 0.605. In the insets the long-time part of the same data are shown.

The full lines in Figs. 1b and c indicate the time dependence of molecular uptake to be expected for a diffusion-limited process via the corresponding solution of Fick's 2nd law [7, 59, 60] with the diffusivity, as measured independently by PFG NMR (values from Fig. 1a). Before the onset of hysteresis, the analytical prediction of molecular uptake is found to be in excellent agreement with the experimental data. This is by no way the case anymore in the range of hysteresis. In fact, here molecular uptake is found to follow an equation of the form [31]

$$\theta(t) = K\theta_{\mathrm{diff}}(t) + (1-K)(\theta_{\mathrm{eq}} - (\theta_{\mathrm{eq}} - \theta_0)\exp\Big(-\big(\ln(t/\tau_0)/\ln(\tau_a/\tau_0)\big)^p\Big). \tag{4}$$

The logarithmic time dependence in the exponent on the right-hand side of eq.(4) is thus found to provide an appropriate mathematical expression of the dramatic slowing down of uptake kinetics. In fact, it is due to this reason that, in a laboratory time scale, the amount adsorbed remains essentially unchanged. The hysteresis data are, therefore, meaningful experimental quantities which may be reproduced with essentially perfect precision. As the physical origin of this dramatic change in the time dependence one has to realize that, with the onset of hysteresis, the limiting process in molecular uptake, obviously, is not anymore the rate of propagation of the individual molecules. Attainment of an eventual equilibrium has now to be associated with the net shift of molecular assemblages, which proceeds under a completely different horizon of time. In fact, the experimentally observed logarithmic dependence has already been proposed as a possible consequence of this novel situation [61, 62].

3.2 Probing the Existence of an Unlimited Number of Different States under Identical External Conditions

The existence of two, quite different states on the adsorption and desorption branches of sorption hysteresis has to be attributed to the existence of two local minima in the Free Energy which determine the respective states of the guest molecules. There is, clearly, no reason to assume that these two states represent the only local minima in the Free Energy landscape. Again, diffusion measurements prove to be a most sensitive tool for probing these different states [63]. As an example, Fig. 2 represents similar data as those shown in Fig. 1a. However, in addition to the data characterizing the situation of conventional hysteresis, Fig. 2 also displays the results of so-called scanning sorption experiments. As an example of this type of measurement, fig. 2a also shows the guest concentrations on the desorption branch, when adsorption has been switched to desorption already before complete saturation, namely in one series of experiments at a relative pressure of $P/P_{\mathrm{s}} = 0.68$ (squares) and in the other at $P/P_{\mathrm{s}} = 0.65$ (triangles). Fig. 2b shows the diffusivities measured at each individual point of the scanning curves.

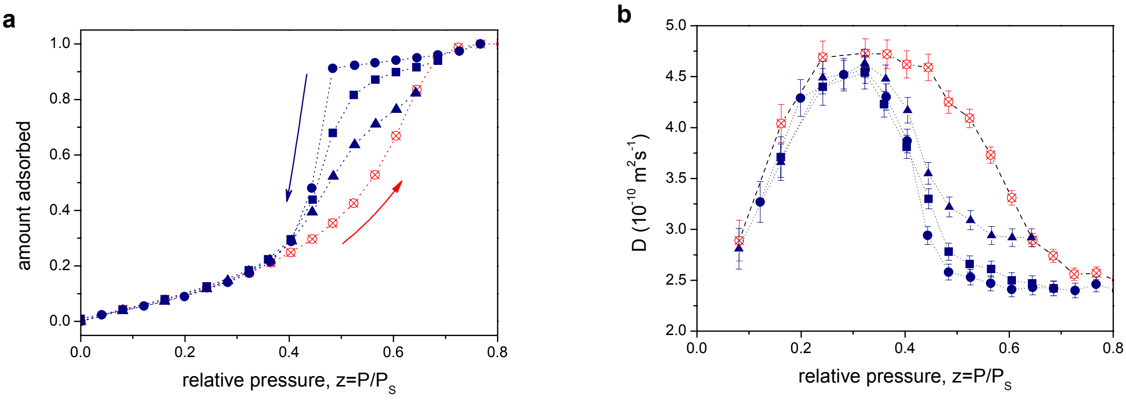

Fig. 2. The relative amount adsorbed (a) and corresponding diffusivities (b) of cyclohexane in Vycor porous glass at T=279 K as a function of the relative pressure z. The open and filled circles show the data obtained on the complete adsorption and desorption branches by a pressure increase from zero to P_s and from P_s to zero, respectively. The triangles and squares give the results of desorption scanning experiments, where pressure was first increased from zero to z=0.68 (squares) and to z=0.65 (triangles) and then the corresponding data were measured upon reducing pressure to zero. The lines are shown to guide the eye.

There is a clear tendency that, at a given pressure, the diffusivities decrease with increasing loading. This is exactly the expected situation since, under the chosen conditions, molecular propagation is known to be much more efficient in the gas than in the liquid phase [64, 65].

In Fig. 3, via Fig. 2a, the diffusivities of Fig. 2b are redrawn as a function of the amount adsorbed. Fig. 3 contains further diffusivities which have been measured during a complete adsorption-desorption cycle of scanning curves [63]. It is worthwhile to emphasize once again that the diffusivities shown in this figure are attained under quasi-equilibrium conditions. This means: repetition of the measurements after a couple of hours (clearly, under strict maintenance of temperature and pressure) leads to exactly the same diffusivities. Thus, PFG NMR provides immediate and unequivocal evidence that, depending on the "history", one and the same number of molecules (since nothing else means a fixed value of the relative pore loading) may be subjected to quite different rates of molecular propagation. Since it is the actual state of the guests within the host system, which determines their diffusivities, differences in the observed diffusivities indicate differences in the states. Since the diffusivities remain constant in the course of (at least) hours, also the respective states are found to be stable over such long intervals of time - irrespective of the fast internal movement of each individual guest molecule.

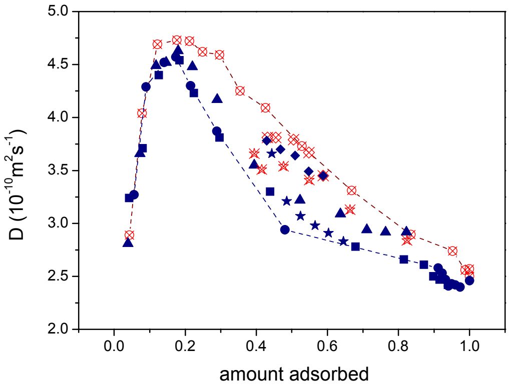

Fig. 3. The diffusivities from Fig. 2b plotted versus the relative amount adsorbed using the data of Fig. 2a. Also diffusivities obtained more complex cycles of the pressure variation are shown.

Again, the trend in the diffusivities may be rationalized by the microscopic situation in the host-guest system. During desorption, cohesion between the guest molecules leads to smaller densities of the liquid phase in the pore space. For identical loadings this, in turn, results in a larger liquid-phase volume fraction and, hence, in a reduction of the contribution of the free pore space to overall molecular transport.

4. Conclusions

PFG NMR diffusion measurements contribute with a completely novel type of information to the current, most vivid discussion of the guest structure and dynamics in nanoporous host systems. We have provided two examples in which the diffusivities serve as sensitive probes of the state of molecular ensembles under confinement. Most importantly, depending on the history, for even identical external conditions, quite different states may thus be shown to remain stable over essentially unlimited intervals of time. Future work has in particular to explore the options of a quantitative correlation between the different states of the gust ensembles and the associated molecular mobilities as directly accessible in the PFG NMR experiments.

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