LETTERS

Exploration of molecular dynamics during transient sorption of fluids in mesoporous materials

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In recent years, considerable progress has been made in the development of novel porous materials with controlled architectures and pore sizes in the mesoporous range[1–4]. An important feature of these materials is the phenomenon of adsorption hysteresis: for certain ranges of applied pressure, the amount of a molecular species adsorbed by the mesoporous host is higher on desorption than on adsorption, indicating a failure of the system to equilibrate. Although this phenomenon has been known for over a century, the underlying internal dynamics responsible for the hysteresis remain poorly understood[5–9]. Here we present a combined experimental and theoretical study in which microscopic and macroscopic aspects of the relaxation dynamics associated with hysteresis are quantified by direct measurement and computer simulations of molecular models. Using nuclear magnetic resonance techniques[10–14] and Vycor porous glass[15,16] as a model mesoporous system, we have explored the relationship between molecular self-diffusion and global uptake dynamics. For states outside the hysteresis region, the relaxation process is found to be essentially diffusive in character; within the hysteresis region, the dynamics slow down dramatically and, at long times, are dominated by activated rearrangement of the adsorbate density within the host material.

The measurement of gas adsorption is a classical characterization technique[3] that remains of enormous importance in the development of new kinds of porous materials with applications in areas ranging from separation and catalysis to microelectronics[4]. The shape of an adsorption isotherm reflects the interactions of the adsorbed molecules with the porous material surfaces, as well as the effect of confinement on the adsorbed fluid properties. For mesoporous materials, an important feature of such measurements is the occurrence of hysteresis at temperatures below the bulk critical temperature. This is widely assumed to be associated with the formation of a condensed liquid-like state[3,5], and represents a possible example of the influence of spatial confinement on a phase transition[5,17]. However, recent mean-field density functional theory studies of a disordered lattice-gas model suggest that hysteresis can occur even though the system does not exhibit an underlying phase transition[6,8]. The results of these studies suggest a central role for the internal dynamics of such systems in giving rise to hysteresis.

An important feature of the dynamics of these systems is suggested by the free energy landscape in the hysteresis region that was predicted in theoretical studies[6,8]. For a medium density state of an adsorbed fluid in a material such as Vycor porous glass, there are a very large number of spatial arrangements of the fluid that are consistent with the average density. These states of the confined fluid represent local minima of the free energy, and they are metastable. The approach to equilibrium (a global minimum in the free energy)

at longer times involves transitions between these states via activated barrier crossings, as shown by dynamic Monte Carlo simulations for the lattice model of a fluid in Vycor porous glass[8]. This is an intrinsically slower process than the relaxation through diffusive mass transfer that characterizes the behaviour away from the hysteresis region. The hysteresis is similar to that observed in disordered ferromagnets as modelled by the random-field Ising model[18], and the dynamical behaviour resembles that predicted for this model[19,20]. In contrast to the abundance of experimental data on adsorption equilibria and hysteresis[1,3,5], there is a striking lack of experiments probing the dynamics. In this Letter, for the first time to our knowledge, a self-consistent set of experimental data on dynamics and transport is presented and used to test the conclusions emerging from these theoretical studies.

We have used nuclear magnetic resonance (NMR) as a probe of the adsorbed fluid[10,11], which allows us to study both the dynamics of adsorption and desorption and the self-diffusivity. Self-diffusion characterizes random translational motion of molecules under equilibrium conditions. It is driven by the internal kinetic energy of the molecules, making it sensitive to various molecular interactions. The self-diffusion coefficient D relates molecular mean-squared displacements $<r^2>$ to the observation time t via Einstein's relation $<r^2> = 6Dt$. In porous materials, D is affected by the restrictions imposed by confinement[21]. Importantly, an inhomogeneous distribution of the adsorbate inside the porous material may also affect its dynamical properties. The spatial variation of the adsorbed fluid density leads to varying local diffusivities. The experimentally measured diffusivity is a quantity averaged over distances exceeding by far the typical size of the inhomogeneities, which is appropriate for the present work. Thus, it may be exploited as a parameter characterizing the adsorbate state in mesopores under different conditions[13,14]. Transient sorption, on the other hand, reflects collective dynamics of molecules under non-equilibrium conditions[21].

Among various experimental techniques for studying self-diffusion, pulsed field gradient NMR is the most suitable for fluids in porous materials[11,21]. This method is based on the creation of an initial coherence of the nuclei and on following its loss in an applied magnetic field gradient due to displacements of the nuclei. Thus, the characteristics of molecular motion may be directly followed over a broad timescale from milliseconds to seconds. At the same time, the initial coherence leads to an observable NMR free induction decay (FID) signal, which is proportional to the number of nuclei in the sample, that is, the amount adsorbed. Thus, transient uptake and molecular diffusion may be probed simultaneously.

In Fig. 1 are shown the adsorption isotherm for cyclohexane in Vycor porous glass and the corresponding diffusivities measured at different points of the isotherm. The amount adsorbed is given in the

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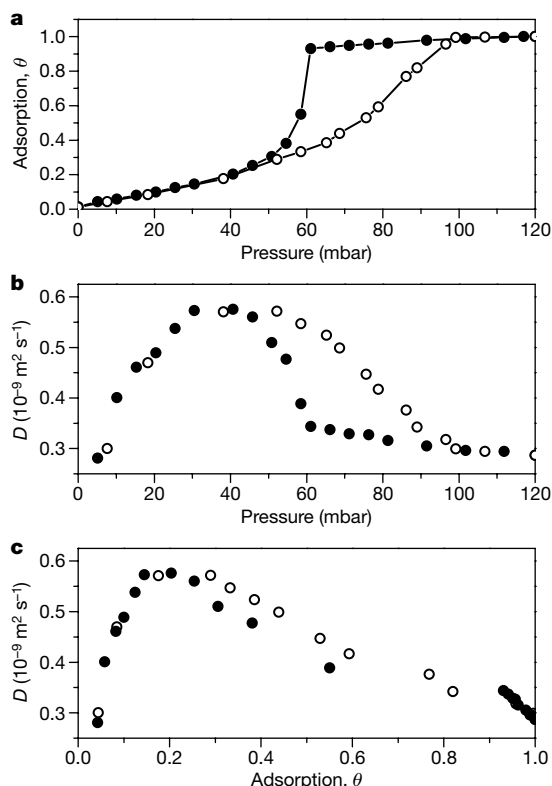
Figure 1 | Experimental adsorption isotherm and effective diffusivities of cyclohexane in Vycor porous glass. a, b, Normalized adsorption θ (see Methods for details) of cyclohexane in pores of Vycor porous glass (**a**) and the diffusivity D (**b**) measured as a function of external vapour pressure P on the adsorption (open symbols) and the desorption (filled symbols) branches of the isotherm at $T = 297$ K. Error bars (s.d.; not shown) are of the order of two symbol heights. The diffusivities were measured using an observation time $t_d = 10$ ms. No dependence of D on t_d in the range 2–300 ms was observed. **c,** Combination of the data of **a** and **b** to show D as a function of concentration.

fraction θ of complete pore filling (details are given in the Methods section) and is referred to as concentration. The observed hysteresis (Fig. 1a) is of the so-called H2 type[3], which is typical of Vycor porous glass. As the diffusivities depend on concentrations, and

concentrations depend on pressure, a plot of diffusivities versus pressure should likewise exhibit hysteretic behaviour (Fig. 1b). Following refs 13 and 14, the observed diffusivities may be satisfactorily predicted by a simple gas kinetics approach involving both surface diffusion and Knudsen diffusion in the free pore space. Remarkably, on plotting D versus θ (Fig. 1c), we see that the hysteretic behaviour is preserved. Evidently, depending on the history through which a particular state was attained—even at equal pore concentrations in the region of the irreversible sorption—the dynamical properties of the adsorbate can be different. In this sense, different values of D at other equal conditions (temperature, concentration) may be considered as a manifestation of the history-dependent adsorbate distribution.

In addition to these experiments, we have made calculations of the adsorption and self-diffusion for the lattice gas model of a fluid in Vycor (see Methods for details), following the procedure given in refs 8 and 22. The resulting isotherms and diffusivities for two different surface–fluid interaction strengths are shown in Fig. 2. Notably, the experimentally observed trends in Fig. 1 are qualitatively well reproduced in the simulations (a more quantitative agreement might be achieved by adjusting interaction parameters in the model, but it is the qualitative behaviour that concerns us here). The effect of the surface interaction on the resulting patterns of the diffusivity is discernible. Apparently, the experiments and model calculations yield a qualitatively consistent picture of the equilibrium dynamics, which we can use as a basis for analysing the transient behaviour.

In Fig. 3, the results of the transient sorption measurements are correlated with the information from the diffusion studies. The figure presents typical examples of the uptake kinetics following a relatively small (5 mbar) stepwise change of the external vapour pressure (Fig. 3a refers to the out-of-hysteresis region and Fig. 3b to the hysteresis region). With the independently known diffusivities and by assuming that diffusion is the rate-limiting process, one may find the uptake function, $\theta_{\text{diff}}(t)$, as a solution of Fick's law. For cylindrical geometry of the monolithic Vycor particle used in the present study, the solution is given by[23]

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

where a represents the radius of the cylindrical particle, α_n are the positive roots of the equation $J_0(\alpha a) = 0$, θ_0 and θ_{eq} are the initial and the final concentrations, and J_0 is the Bessel function of the first kind. With θ_{eq} taken from the experimental data in Fig. 3 at long times
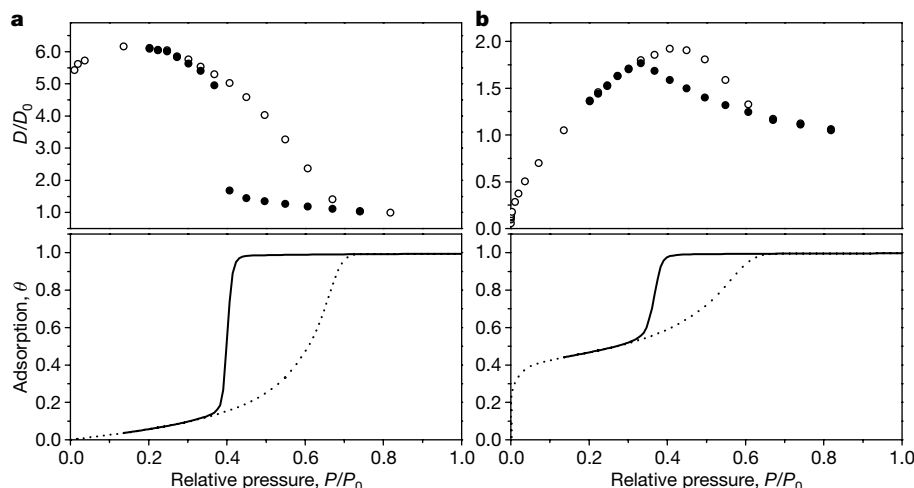

Figure 2 | Simulated adsorption/desorption isotherm and effective diffusivities for a lattice model of a fluid confined in a Vycor porous glass. Lower graphs, adsorption/desorption isotherms (adsorption, dotted line; desorption, solid line), and upper graphs, self-diffusion coefficients (adsorption, open circles; desorption, filled circles), for the lattice model of a

fluid in a Vycor model, calculated by Monte Carlo simulations. **a,** Data for a weak surface interaction ($y = 1$); **b,** data for a strong surface interaction ($y = 3$). Here y is the ratio of the strengths of the solid–fluid and fluid–fluid nearest neighbour interactions in the lattice model.

where the uptake is almost complete, and with D from Fig. 1, $\theta_{\text{diff}}(t)$ is readily calculated, as shown in Fig. 3 by the dotted lines. Importantly, equation (1) with θ_0 and θ_{eq} chosen as described correctly reproduces the experimental data for the region out of hysteresis, but fails in the hysteresis region. Slower equilibration in the hysteresis region has been noted before[9,24,25] but has been interpreted in terms of a decrease in the diffusivity[24,25], based on comparing experimental uptake curves with simple micro-kinetic models. However, what we are seeing here is a fundamental difference in the nature of the relaxation dynamics for states within the hysteresis region compared with those out of this region, and this is not simply a change in the rate of diffusion.

The mechanism leading to the anomalous behaviour in the hysteresis region can be illuminated using the lattice gas model of a fluid confined in Vycor porous glass[8]. Figure 4 shows results from dynamic Monte Carlo simulations of the adsorption versus time for a system quenched into the hysteresis regime, and is in very good agreement with the experimental observation. Detailed analysis of the accompanying data obtained from these calculations allowed us to identify a two-stage mechanism of the transient uptake in the hysteresis region, which may be visualized in the following way. Adsorption at low pressures consists of diffusion of the gas into the pore structure, with the formation of adsorbed layers on the pore walls. In general, the entire pore space is accessible to mass transfer from the bulk, making the dynamics purely diffusive. As the pressure

increases, the average density builds up until it becomes possible for condensation processes to occur, in which liquid 'droplets' appear at various places in the pore structure, forming bridges between the pore walls. The formation of these 'droplets' is initially not driven by a global equilibration process so that the distribution of the fluid density around the system represents a local minimum of the free energy.

Subsequent density redistribution and/or droplet growth are required for relaxation to global equilibrium (at a given external gas pressure), and these are essentially activated processes requiring the crossing of barriers of height[19] $b\xi^\psi > kT$ (where ξ is the characteristic 'droplet' size, $\psi > 1$, k is Boltzmann's constant, T is temperature, and b is a constant determined by the fluid properties and external conditions). A quantitative description of the relaxation dynamics is suggested by analysis of the critical dynamics of the random-field Ising system[19,20]. The lattice gas model used here can be interpreted as a kind of random-field Ising model with site-dilution[8]. The total relaxation can be represented by a linear combination of two relaxation processes: a diffusive one given by equation (1) with the relative weight K and an activated one[20] with the weight $(1-K)$, so that

$$\theta(t) = K\theta_{\text{diff}}(t) + \\ (1-K)\big(\theta_{\text{eq}} - (\theta_{\text{eq}} - \theta_0)\exp\{-[\ln(t/\tau_0)/\ln(\tau_a/\tau_0)]^p\}\big) \quad (2)$$

where τ_0 is the characteristic microscopic time, τ_a is the typical relaxation time for activated dynamics, and p is the parameter reflecting distribution of the barrier heights[26,27]. Such a two-term function with $p = 3$ (refs 26, 27) can be used to give an excellent fit of the $\theta(t)$ results from both experiment and our Monte Carlo simulations. Similar relaxation processes have also been observed in studies of liquid–liquid phase separation in Vycor porous glass[27].

In conclusion, the extremely slow relaxation inherent to activated dynamics governs the approach to equilibrium in the hysteresis region at longer times. This explains why hysteresis, although representing a departure from equilibrium, is so reproducible in experiments. The convergence of experiment and theory shown here represents a major step forward in understanding the fundamentals of relaxation phenomena in confined fluids. At the same time, correlating diffusion and relaxation in porous materials represents an important approach for the exploration of the internal dynamics in mesoscopic systems. Continuation of these studies with tailor-made materials, spanning the total range of pore architecture between the
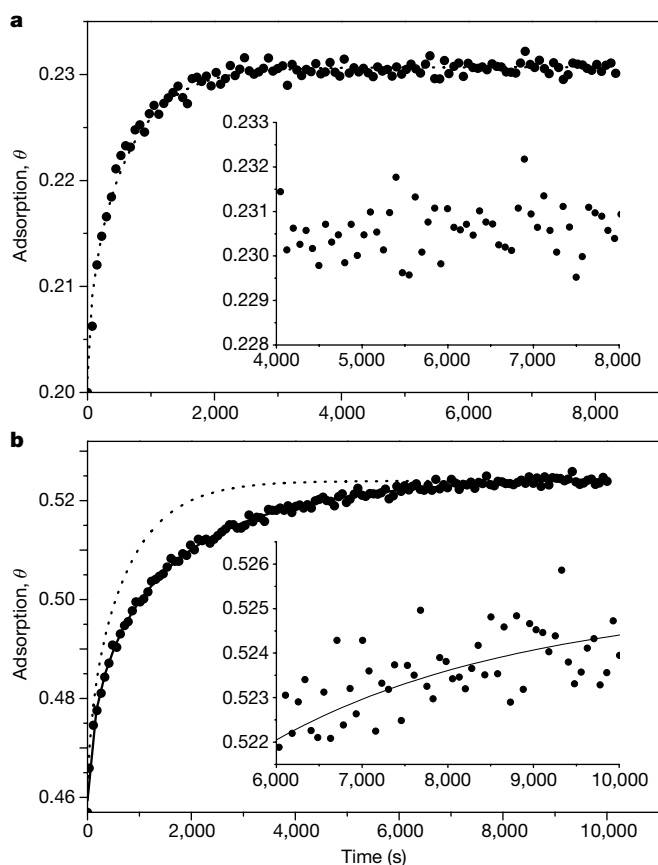
Figure 3 | Experimental transient sorption of cyclohexane in Vycor porous glass. a, b, Typical adsorption kinetic data (points) obtained upon stepwise change of the external vapour pressure from 40 mbar to 45 mbar (**a**) and 70 mbar to 75 mbar (**b**). Insets show the long-time part of the same data; axis quantities and units are the same as the main figures. The experimental data of the adsorption branch of the isotherm shown in Fig. 1 represent the θ_{eq} values at the longest observation time ($t \approx 10^4$ s). The dotted lines in the figures show the kinetics calculated using equation (1). The solid line in **b** and in the inset shows results from equation (2) with parameters $\tau_0 = 600$ s, $\tau_a = 4{,}540$ s, $K = 0.8$ and $p = 3$.
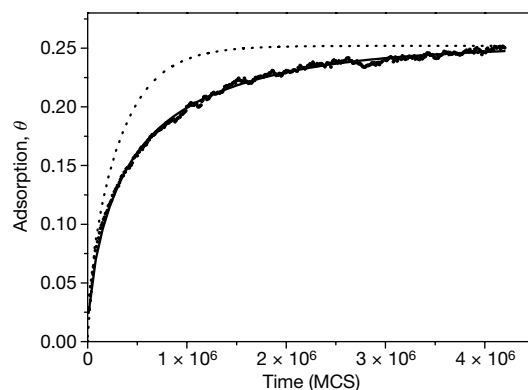
Figure 4 | Simulated transient sorption for a lattice model of a fluid confined in Vycor porous glass. Graph shows density versus time from a dynamic Monte Carlo simulation of the uptake of a fluid into a Vycor glass in the hysteresis regime. Simulations have been performed for a weak surface interaction $y = 0.7$, where y is the ratio of the strengths of the solid–fluid and fluid–fluid nearest-neighbour interactions in the lattice model. Time is given in Monte Carlo steps (MCS). The broken line is a fit to the short-time behaviour (diffusion model). The solid line is from equation (2) with parameters $\tau_0 = 1.4 \times 10^5$ MCS, $\tau_a = 2.6 \times 10^6$ MCS, $K = 0.68$ and $p = 3$.

limiting cases of straight channels[14] and hollow-sphere arrangements[28], should lead to a range of additional insights, including a more complete understanding of the effect of the porous material geometry on the relaxation dynamics.

METHODS

NMR experiments. The experimental set-up used in the present study consists of an NMR glass tube containing the porous material, connected through a valve to a large reservoir with the bulk vapour phase of the fluid under study. As a porous host, a Vycor porous glass particle in the form of a cylinder of 3 mm diameter and of 12 mm length has been used. The internal porous structure of the particle consists of a disordered network of interconnected pores with an effective diameter of about 6 nm (refs 15, 16). The volume of the gas reservoir significantly exceeds that of the porous material. The vapour pressure can be varied from millibars to the saturated vapour pressure P_0 of the liquid under study. After setting a certain pressure in the reservoir, opening the valve causes a stepwise change of the external conditions for the porous material. A subsequent equilibration of the intra-pore density was followed by recording the NMR FID signal intensity S_{FID} as a function of time. In order to avoid the necessity of calibrating the measured NMR signal, we confine ourselves to presenting a normalized value, the relative intra-pore concentration $\theta = [S_{FID}(P)]/[S_{FID}(P_0)]$, where $S_{FID}(P_0)$ is the signal intensity measured at full saturation of the pores. The self-diffusion coefficients D were measured at sufficiently long times after the pressure change when no notable change of the amount adsorbed was observed. **Lattice model simulations.** In the model used here, the positions of the adsorbed molecules and the porous solid are given by occupying the sites of a cubic lattice (either simple cubic or face-centred cubic). The positions of the solid sites are fixed, and chosen by coarse-graining the solid distribution obtained from the gaussian random field model of the interfacial structure generated in the phase separation process occurring in the preparation of the porous glass[8,29]. The adsorption/desorption isotherm was calculated using Monte Carlo simulations[30] in the grand canonical ensemble. The self-diffusion was simulated using Kawasaki dynamics, a process in which molecules hop to adjacent sites on the lattice following the Metropolis criterion for accepting the new configurations generated[30].

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