Probing Memory Effects in Confined Fluids via Diffusion Measurements

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Confinement of fluids in porous materials is widely exploited in a variety of technologies, including chemical conversion by heterogeneous catalysis and adsorption separations. Important fundamental phenomena associated with many-molecule interactions occur in such systems, including a remarkably long “memory” of the past when the actual amount of molecules in the pores dramatically depends on the history of how the external conditions have been changed. We demonstrate that the intrinsic diffusivity as measured by NMR serves as an excellent probe of the history-dependent states of the confined fluid. A remarkable feature of our results are differences in diffusivity between out-of-equilibrium states with the same density within the hysteresis loop. This reflects different spatial distributions of the confined fluid that accompany the arrested equilibration of the system in this region.

A critical component of the processing of raw materials into value-added products involves conversion by heterogeneous catalysis and chemical separation by molecular sieving and selective adsorption in porous materials. In all cases, the use of nanoporous catalysts and adsorbents ensures a particularly intimate interaction between the guest molecules and the internal surfaces of the host system, which gives rise to the desired processes. Recent developments in chemistry and materials science are making it possible to tailor the chemistry and nanostructure of porous materials to optimize their performance in specific catalytic and separations applications, with new applications ranging from small-scale electronics, to sensors, to diagnostic devices. Simultaneously, with the advent of advanced materials, including those with highly ordered pore structure, there is an increasing focus on defining the nature of fluid (liquid or gas) systems under confinement and how these systems evolve as a result of changes in state. A related problem of interest is the interface between states of different density for confined fluids.

Confined fluids may exhibit a range of states that are not seen in bulk fluids because changes in state of bulk fluids is often limited to transitions between the liquid and vapor states, and the interface between the confined fluid and the bulk phase is not well defined. In the confined system, the density distribution is expected to depend on the history of the state of the fluid. This is analogous to the liquid and vapor states of bulk fluids, but does not tell us anything about the density distribution within the system. In this report, self-diffusion measurements by pulsed field gradient nuclear magnetic resonance (PFG NMR)19 are used to probe the state of a fluid (cyclohexane) confined within the internal pore space of a model porous material, namely Vycor porous glass. We provide direct experimental evidence that states of the confined fluid that accompany the arrested equilibration of the system in this region.

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The end of the hysteresis loop on adsorption, namely at 0.68. The results of measurements where pressure was reduced before adsorption/desorption measurements. Recent theoretical analyses show that the cyclohexane molecules in the pores are normalized to the value at a mean pore diameter around 5 nm. NMR provides the possibility to probe the amount adsorbed as function of time as well as the self-diffusivities. The former has been measured by following the NMR free induction decay signal intensity, which is directly proportional to the number of nuclei in the sample. The self-diffusivities have been measured by means of PFG NMR using a home-built NMR spectrometer. All measurements have been performed at 297 K.

The primary data emerging from our experiments are plotted in Figures 1 and 2. Figures 1a and 2a show the conventional adsorption and desorption isotherms, namely, the amount θ of cyclohexane molecules in the pores normalized to the value at saturation pressure Pₛ as a function of the relative pressure, P/Pₛ, together with some sample adsorption and desorption scanning curves within the hysteresis loop. The data obtained on the complete adsorption branch (open circles, pressure increasing from zero to Pₛ) and desorption branch (filled circles, pressure decreasing from Pₛ to zero) clearly reveal a so-called hysteresis loop (for 0.4 < P/Pₛ < 0.75). In addition, Figure 1a also shows the results of measurements where pressure was reduced before the end of the hysteresis loop on adsorption, namely at 0.68 Pₛ (squares) and 0.65 Pₛ (triangles). These are examples of desorption “scanning curves”. Figure 2a displays data obtained when the desorption scanning curve (filled triangles) was not continued to pressures below the hysteresis range. The open triangles in Figure 2a reveal the situation when, after the pressure reaches 0.44 Pₛ, the scanning desorption curve (which started at 0.65 Pₛ) is reversed into an adsorption scanning curve. Similarly, the squares in Figure 2a show the situation when an incomplete adsorption scanning sequence (open squares) is followed by the desorption scanning sequence (filled squares).

Our density versus pressure results are consistent with previous adsorption/desorption measurements. Recent theoretical analyses using mean field theory and Monte Carlo simulations provide an understanding of the observed behavior in terms of the total probability distribution of molecular displacements (the “propagator”), via the spin–echo diffusion

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and gaseous phases). This allows a straightforward explanation of the dependence on the square of the applied magnetic field gradient attenuation functions, which were found to exhibit an exponential dependence on the square of the applied magnetic field gradient strength, revealing clear evidence of a Gaussian propagation. In turn, this implies fast exchange between different regimes of molecular mobility (namely, in the capillary-condensed, adsorbed, and gaseous phases). This allows a straightforward explanation of the general trends in the diffusivities. We can identify three main contributions to the average self-diffusivity in the system. A slow diffusion contribution from fluid in close contact with the pore walls makes its largest fractional contribution to the average diffusivity at low pressures. A second fast diffusion contribution comes from the gas-like fluid at the center of the pores away from the pore walls, making its largest fractional contribution to the average diffusivity over an intermediate range of pressure. Finally a slow diffusion contribution from fluid in liquid-like states at the center of the pores makes its largest fractional contribution at high pressure. In nice agreement with this view, the diffusivities on the adsorption branches notably exceed those on the desorption branches. This is a consequence of the fact that, at a given pressure, during desorption conditions a larger fraction of molecules occurs in the less-mobile liquid phase than during adsorption. The most important feature of our results emerges when the diffusivity data from Figures 1b and 2b are plotted versus the relative pressure. The filled squares show the data obtained for the desorption scan from 0.65 \( P \) to 0.44 \( P \), followed by an adsorption scan from 0.44 \( P \) to 0.65 \( P \), respectively. The open and filled squares refer to the data obtained in an adsorption scan from 0.43 \( P \) to 0.59 \( P \), followed by a desorption scan from 0.59 \( P \) to 0.43 \( P \), respectively.

Figure 2. The same as in Figure 1, but the data are obtained using more complex adsorption and desorption cycles. The open and filled circles are the data on the complete adsorption and desorption from Figure 1. The filled squares show the data obtained for the desorption scan from 0.65 \( P \) to 0.44 \( P \), followed by an adsorption scan from 0.44 \( P \) to 0.65 \( P \), respectively. The open and filled squares refer to the data obtained in an adsorption scan from 0.43 \( P \) to 0.59 \( P \), followed by a desorption scan from 0.59 \( P \) to 0.43 \( P \), respectively.

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Figure 3. The diffusivities in Figures 1b and 2b plotted versus the amount adsorbed \( \theta \) from Figures 1a and 2a demonstrating different diffusivities for states with the same density. The filled squares show the data obtained for the desorption scan from 0.44 \( P \) to 0.43 \( P \), followed by an adsorption scan from 0.43 \( P \) to 0.65 \( P \), respectively. The open and filled squares refer to the data obtained in an adsorption scan from 0.43 \( P \) to 0.59 \( P \), followed by a desorption scan from 0.59 \( P \) to 0.43 \( P \), respectively.

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total sample since the propagator results as an ideal Gaussian. This means that, over distances of more than about 1 µm as the typical molecular displacements traced in our experiments, we do have all over the sample completely identical filling properties. Otherwise, we should have observed a distribution of diffusivities. This rules out the idea that emptying of the porous space proceeds via gas invasion, i.e., beginning at the glass boundary and gradually percolating into the sample interior. However, interplay between pore-blocking and cavitation may effect that, during desorption, more extended regions of the liquid and gaseous phase are formed than during adsorption. We anticipate that the former case yields slower diffusivities due to tortuosity. The relevance and relative impacts of these two effects are accessible by computer modeling. This work is under progress.

Besides this general tendency in the “history dependence” of the diffusivities for a given overall concentration, one clearly has to be aware of further influences related to the differences in the density distribution within the porous space. They ultimately correspond to the differences in the system’s history, e.g., in the way the external pressure has been varied to attain exactly the given state. We note that, as revealed by the constancy of the measured diffusivities over time periods from hours to days, these different states are preserved over essentially unlimited intervals of time. The diffusivities presented by Figure 3 indicate the existence of several different states at one and the same loading. Further states, however, may of course be reached by choosing further ways of system preparation. Within each of these states, the confined fluid molecules rapidly vary their positions as reflected by their diffusivities. Importantly, the molecular displacements recorded during typical PFG NMR observation times on the order of milliseconds exceed the typical pore size by more than 2 orders of magnitude. Thus, within the high-dimensional phase space formed by spatial and kinetic coordinates of all molecules, the molecular trajectories within these different states define subspaces strictly separated from each other. This separation occurs irrespective of the dramatic rate of molecular redistribution within the system. This means that this separation can only be eliminated by collective effects.

The overall diffusivity has thus been identified as a sensitive probe of the given state of a confined liquid. Different states emerge from the different history of the system. They are associated with different out-of-equilibrium distributions of the fluid within the pore network, which, in turn, give rise to different overall mobilities of the system. Being separated by large barriers in the system free energy, these states are found to remain stable over very long intervals of time. We have created quite different series of states by appropriate variation of the pressure regime in the surrounding atmosphere, reflected by a corresponding spectrum of diffusivities. Large time-span observation of such diffusivities opens a novel route of experimentally exploring the time evolution of fluid states under confinement.

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