

Memory Effects in Confined Fluids via Diffusion Measurement

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1. Introduction

For bulk fluids it is always possible to establish the state of the equilibrium coexistence between vapour and liquid phases by putting these phases in contact. In contrast, the fluids confined in mesoporous matrices can reside in different quasi-equilibrium coexistence states for very long periods of time. The transition between these metastable states occurs via changes in the driving force (pressure or chemical potential, temperature of the bulk phase) or via the thermally induced fluctuations of the fluid. The latter process is generally accompanied by very large barriers in free energy and may result in the occurrence of the so-called adsorption hysteresis.

The hysteresis is a well-known feature of adsorption/desorption isotherms for light gases, such as nitrogen, at cryogenic temperatures. Depending on the pore structure of the adsorbent, it may involve the existence of a very large number of completely reproducible but non-equilibrium states that are accessible via scanning sorption experiments, i.e. various cycles of incomplete filling/draining procedures. Traditional adsorption measurements give the relationship between the confined fluid density and the bulk chemical potential (via the bulk pressure) but do not provide detailed information about the density distribution within the system.

2. Experiment

In this work, self-diffusion measurements by means of pulsed field gradient nuclear magnetic resonance (PFG NMR) 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 possessing random pore structure with an average pore diameter of about 6 nm.

The molecular self-diffusivities have been measured along with the adsorption/desorption isotherms. The same type of measurements has been also performed during scanning sorption experiments. Fig. 1 shows the major adsorption and desorption isotherms, which

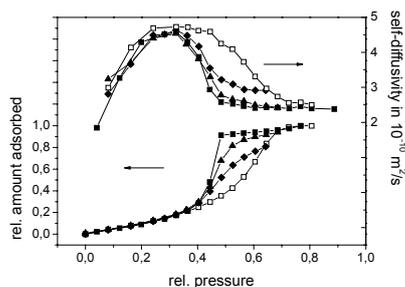


Fig.1: The relative amount adsorbed (bottom) and the corresponding self-diffusivities (top) of cyclohexane in Vycor at 297 K as a function of rel. pressure. Major adsorption (□) and desorption (■) isotherms envelop the scanning curves (◆,▲)

envelope desorption scanning curves. Additionally, the figure demonstrates the respective self-diffusivities, measured simultaneously with the amount adsorbed at the equilibrium after every pressure step.

The qualitative behavior of the self-diffusivities may be explained in terms of the effective self-diffusivity which consists of contributions from the liquid and gas phases [1]. It can be shown that the isotherms of the self-diffusivities are directly related to the sorption isotherms.

The most important feature of the experimental results shown in Fig. 1 arises when the self-diffusivities are re-plotted as a function of amount adsorbed, i.e. the number of molecules. These data are presented in Fig. 2 [2]. Remarkably, the same amount of molecules adsorbed in the porous matrix exhibit different self-diffusivities dependent on the history, how the state has been attained!

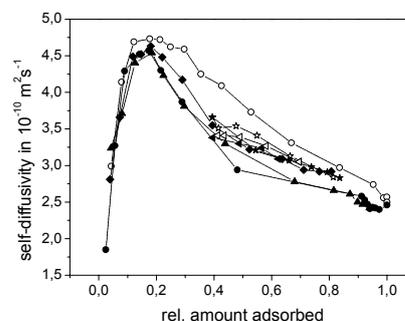


Fig. 2: Diffusivities of cyclohexane in Vycor at 297 K plotted versus rel. amount adsorbed. Additional data are taken from further scanning curve experiments [2].

2. Conclusions

We provide direct experimental evidence that, within hysteresis loops, states with the same average fluid density may have different average self-diffusivities. These differences reflect differences in the density distributions between the states. Thus, molecular diffusivity is shown to be an excellent probe of the history-dependent states of the confined fluid [2]. The self-diffusivities reflect different arrested spatial distributions of the confined fluid that accompany the very slow equilibration of the system in this region [3].

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