New perspectives on anomalous dynamics during sorption hysteresis

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The adsorption hysteresis phenomenon is a classical example of a mesoscalic confinement effect upon macroscopical properties of fluids. It has been recently suggested that the history-dependent character of the adsorbate accommodation in random nanoporous structures may result from a rugged free energy landscape with many local minima separated by free energy barriers [1]. As it was inferred from computer simulation studies [2], activated crossing of these barriers leads to an extremely slow relaxation to the equilibrium state. In the present work, these predictions have been addressed experimentally using NMR methods.

Based on a self-consistent set of experimental data provided by NMR, namely on adsorption kinetics at different pore fillings and corresponding local self-diffusivities measured independently, the anomalously slow intra-pore density relaxation in mesoporous glasses with random porous structure has been proved in the hysteresis region. At the same time, in the out-of-hysteresis region, as expected, the density relaxation has been measured to be diffusive. The observed slowing down of the density relaxation is discussed in the frame of a random field Ising model with a non-conserved order parameter [3], which has been successfully used to describe critical phenomena of binary liquids in random glasses [4].

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