Metastable Confinement of Molecular Hydrogen in Double Wall Carbon Nanotubes bundles

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Carbon nanostructured materials are regarded to have high potential for the storage and management of H_2 at cryogenic temperatures, and so they are of an outstanding practical importance. H_2 has many advantages as energy vector but an efficient storage is technologically challenging since the needed physical conditions are demanding even at a theoretical level. For instance, the strong quantum character of the H_2 molecule and its condensates leads to theoretically unexpected behaviours under confinement [1]. During our search for materials and processes of interest in energy applications, we have observed isothermal large hysteretic hydrogen adsorption in samples made out of Double Wall Carbon Nanotubes bundles at 50 K, 77 K and 150 K and up to 15 bar of pressure (see Figure 1). Adsorption metastability opens remarkable possibilities: it can be used to lower the working pressure for a given uptake; to increase the usable capacity; or to facilitate thermal management – see Ref. [2] for the analogous situation with methane. The case of metastable H_2 adsorption has been barely explored, mostly in the context of Metal-Organic Frameworks (MOFs) as adsorbents [3] and linked to structural deformations of the frameworks. For nanostructured carbons, hysteresis has been associated with chemisorption in metallic particles [4], characterized by undesirably high desorption energy barriers. In order to gain information about the microscopic spatial structure and dynamics of the observed phenomenon we made a series of inelastic neutron scattering measurements at various temperatures and H_2 loads. The elastic signals (diffraction) at different H_2 loads are consistent with the uptake of the H_2 within the interstitials of the bundles. The quasielastic signal (centred around the null energy transfer) display an anomalous dependence on momentum transfer (i.e., in spatial correlations) which is nicely reproduced by an accurate 1D dimensional diffusion model (as expected from interstitial confinement of the H_2 fluid) while the complete inelastic signal precludes the possibility of chemisorption onto the sample metallic impurities. Once discarded a chemisorption mechanism, we developed a 2D dimensional model that allowed us to restrict the parameters space and the computational times to a feasible size (Figure 2). The 2D model reveals a narrow range of microscopic parameters where the hysteresis shows up as the same time nicely reproducing the qualitative behaviour of the real system. The metastability emerges as consequence of the hierarchical structure of energy barriers, a structure that is sensitive to the H_2 uptake through the expansion/contraction of the bundle configuration. Preliminary neutron diffraction results confirm the appearance of this structural hysteresis validating the proposed microscopic mechanisms responsible for the metastability.

REFERENCES

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FIGURES

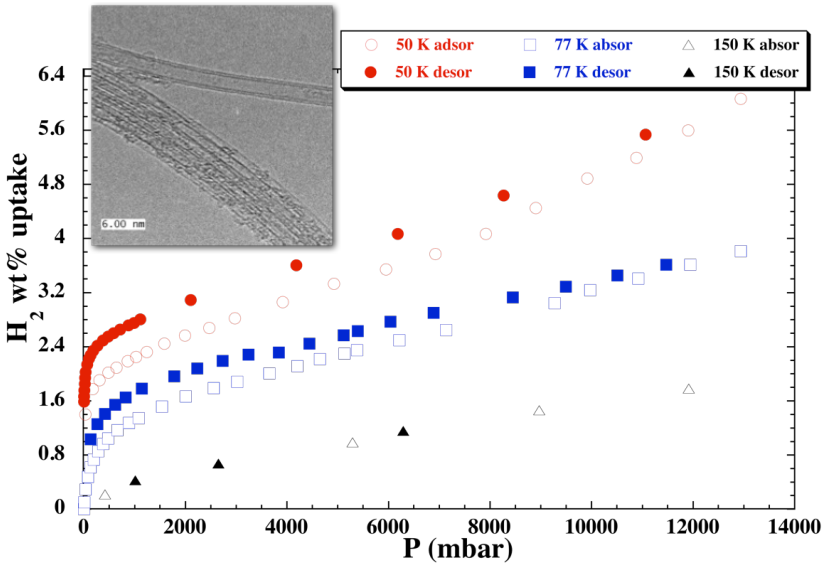

Figure 1: Isothermal H_2 adsorption/desorption cycles in DWCTNs bundles at 50 K, 77 K and 150 K. In the superimposed picture at the left-up corner a transmission electron microscopy image of one of the bundles is shown.

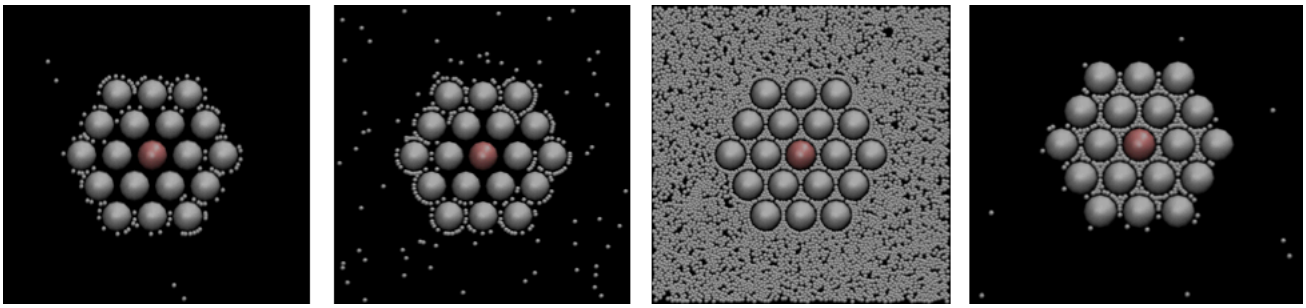

Figure 2: Snapshots of the two-dimensional uptake of H_2 molecular discs (represented by small white spheres) within a bundle of disks (represented by large spheres) along an isothermal adsorption/desorption cycle displaying adsorption hysteresis.