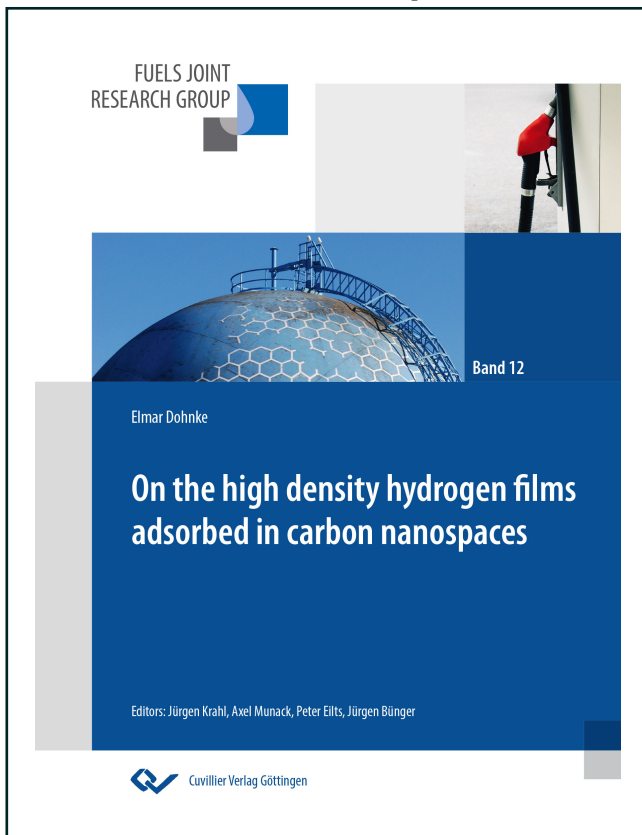




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## On the high density hydrogen films adsorbed in carbon nanospaces



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## Chapter 1 - Introduction

Over the last decade several attempts were made to decrease the carbon dioxide emissions and dependency on fossil fuels for transportation. Alternative fuels, such as natural gas (Methane) or hydrogen are promising candidates in overcoming some of the issues fossil fuels bring. For example, both fuels can be manufactured from renewable sources. In the case of natural gas, both biomass (biological waste) and carbon dioxide can be converted in synthetic natural gas (SNG) by thermo-chemical processes or by Sabatier reaction, respectively[1]. Hydrogen can also be produced from a renewable source, i.e. water. Water is thereby split into hydrogen and oxygen by electrolysis. Both alternative fuels can be manufactured by using alternative energy sources such as solar panels or wind energy, which increase the overall carbon dioxide efficiency.

One major drawback of the alternative fuels mentioned here is their gaseous state at ambient temperature. For example, 4 kg hydrogen occupies a volume of 45 m<sup>3</sup> at atmospheric pressure and temperature[2]. It makes the usage as an alternative fuel in transportation difficult because large onboard storage capacities are needed. There are three ways to overcome this problem. (i) Liquefaction by cooling the gas to cryogenic temperatures is one approach to increase gas storage capacities. For example, the container ship from TOTE runs on liquefied natural gas which is stored at 111 K[3]. Unfortunately, this method requires heavy cryogenic vessels and a high amount of energy for the liquefaction process, which lowers the total energy efficiency of the system. It is therefore not suited for small transportation vehicles such as cars. (ii) The second one, used by Toyota's first commercial hydrogen fuel cell car, is to store the gas under pressures up to 700 bar. Again, this means heavy, bulky onboard tanks are needed. For example, the carbon-fiber tanks used by Toyota have an outer volume of 122 L and weigh 87.5 kg[4]. Additionally, hydrogen needs to be pressurized to 700 bar at the refueling station, lowering the total energy efficiency of the system. (iii) Another way to overcome the storage obstacle is by

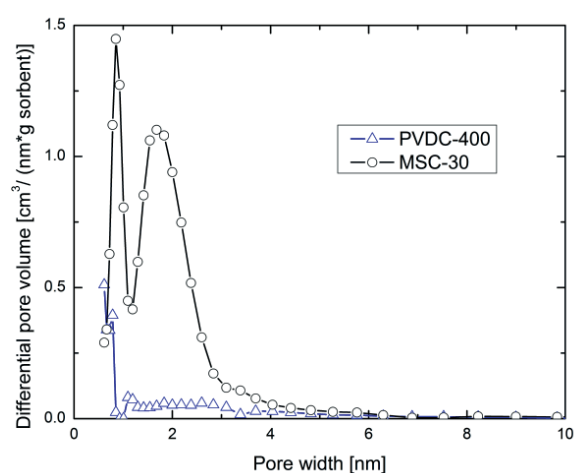


filling the gas tanks with high surface area materials, such as metal organic frameworks (MOFs), activated carbon, or synthetic carbons which densify the gas by adsorbing it at their surface. Therefore these materials reduce the required pressure in tanks without the necessity for cryogenic temperatures, allowing for a smaller, lighter tank design. In physical adsorption, no energy barrier is preventing the molecule from approaching the surface if no diffusional barriers are present. The process does not need activation energy resulting in faster kinetics. Unlike chemisorption, physical adsorption is completely reversible meaning no additional treatment is needed before refiling or during depletion.

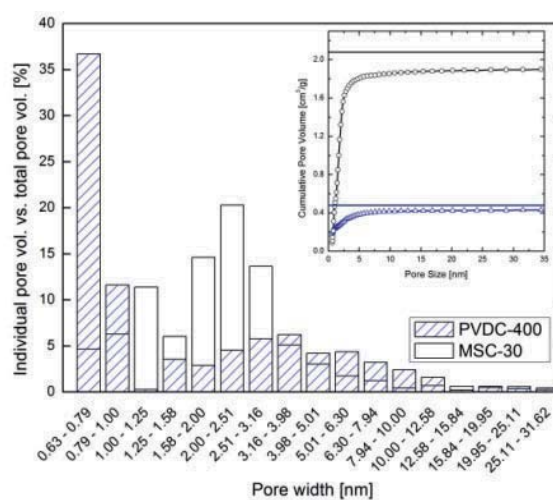
Adsorption materials from metal organic frameworks have been proposed as hydrogen storage materials due to their modular surface chemistry[5]. However, they are costly to produce. These materials can only be manufactured in small quantities involving expensive organic linkers and a multi-step synthesis[6]. Compared to metal organic frameworks, chemically activated carbons are generally cheaper to manufacture because they do not involve expensive chemicals. However, their manufacturing process includes multiple steps and the use of corrosive chemicals, such as potassium hydroxide, at high temperatures, and the product must be washed extensively to remove the remaining potassium hydroxide from the surface[7]. Unlike MOFs and activated carbons, synthetic carbons are easy and cheap to make due to a single step manufacturing process, consisting of heating a polyvinyl chloride based plastic under inert gas. The single step process also means it will be easier to mass produce. This plastic type is widely used as food wrap, which could be recycled for making synthetic carbons.

In addition to being easily manufactured, synthetic carbons also possess a range of properties making them favorable for gas storage. Typical high surface area carbons made by chemical activation processes, such as KOH activation, have a broad distribution of pore widths ranging from 0.8 nm to 12 nm, with the majority being between 0.8 nm and 8 nm. Only a small fraction of its pore volume comes from pores smaller than 1 nm (Figure 1). Conversely, synthetic carbons,

made from Saran<sup>®</sup> (polyvinylidene chloride-co-polyvinyl chloride) or pure polyvinylidene chloride (PVDC), have narrow pore size distributions with the majority of pore widths being smaller than 1 nm. In fact, synthetic carbons have almost 5 times more pore volume from sub-nanometer pores compared with activated carbon (Figure 2). Such narrow pores lead to H<sub>2</sub> adsorption energies as high as 9 kJ/mol, compared to 6 kJ/mol from commercially available activated carbon MSC-30[8]. The enhanced adsorption energy is favorable because it increases the material's capacity for storing hydrogen gas.



**Figure 1** Pore size distribution for PVDC-400 and MSC-30 calculated from quenched solid state functional theory.



**Figure 2** Individual pore volumes and their contribution to the total pore volume.

To improve the materials gas storage capacity it is necessary to understand the mechanisms of gas adsorption in nanoporous materials. We investigate how materials with different pore size distributions and chemical compositions affect the adsorbed hydrogen film under supercritical conditions. Film properties, such as thickness and density, have been estimated by analyzing the high pressure portion of cryogenic isotherms. Additionally, the cross-sectional area of an adsorbed molecule was estimated from the film thickness and specific surface area.

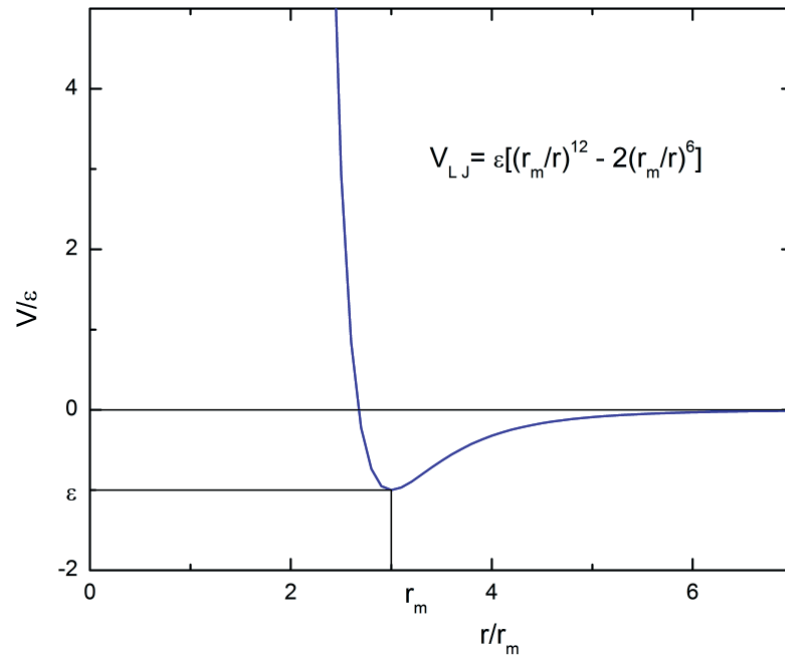


In addition, an attempt was made to estimate the specific surface area from the adsorbed film volume. In contrast to traditional theories such as Brunauer-Emmett-Teller (BET), it neither requires any knowledge about the cross-sectional area of an adsorbed molecule nor makes any assumptions about the packing order of the molecules in the film.

A new high pressure adsorption instrument for cryogenic temperatures was designed to evaluate isotherms at temperatures as low as 7 K and its design and performance has been tested against a commercially available adsorption instrument.

## 1.1 Principles of Adsorption

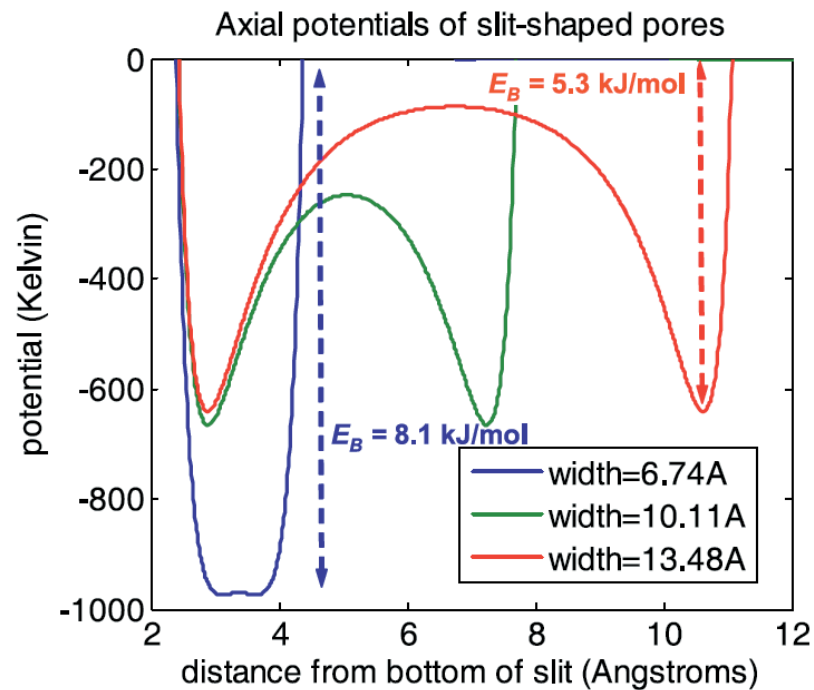
Adsorption is defined as the densification of an adsorbate (i.e. gas or liquid) in the vicinity of a bulk interface (adsorbent) and arises from attractive dispersion interaction (van der Waals force, London force), in combination with short range repulsive interactions, between adsorbent and adsorbate. The resulting potential can be described by the Lennard-Jones potential, also referred as 12-6 potential[9]. It is composed of a long range attractive interaction coming from fluctuations in charge distribution of both the adsorbate molecule and surface molecules, and a repulsive component due to overlapping electron orbitals of the gas molecule and substrate at short distance. This type of interaction hinges on the adsorbent properties, such as surface chemistry or geometry, and the nature of the adsorbate.



**Figure 3** Arbitrary Lennard-Jones potential energy curve as a function of the distance from the sorbent's surface. The minima correspondence to the equilibrium distance between adsorbent and adsorbate.

In narrow pores gas adsorbs strongly due to the overlapping van der Waals potentials coming from both walls and therefore increases adsorption energies. The increase in adsorption energy depends on how much the van der Waals potential overlaps. Molecular dynamics calculations done by J. Burrell et al. predict such a behavior. For example, a slit-shaped pore with a 1.3 nm width has calculated maximum adsorption energy of 5.3 kJ/mol on each wall. It also shows a total of two minima, indicating the adsorbed gas forms one layer on each wall. A 0.67 nm width slit-shaped pore shows only one steep minimum with a calculated adsorption energy of 8.1 kJ/mol (Figure 4)[8]. This indicates hydrogen forms only one dense layer in narrow pores but with higher adsorption energy. Everett and Powl show that pore geometry also has an effect on the potential[10]. In slit-shaped pores two walls contribute to the total potential, while cylindrical pores consist of one surrounding wall leading to a much deeper and stretched out potential. For example, the adsorption energy enhancement in a slit pore with twice the width of the adsorbing

molecule is almost zero, but a similarly sized cylindrical pore has a 50% enhancement. This shows adsorption is much stronger in narrow, cylindrical pores and materials with a majority of such pores are therefore favorable hydrogen storage materials.

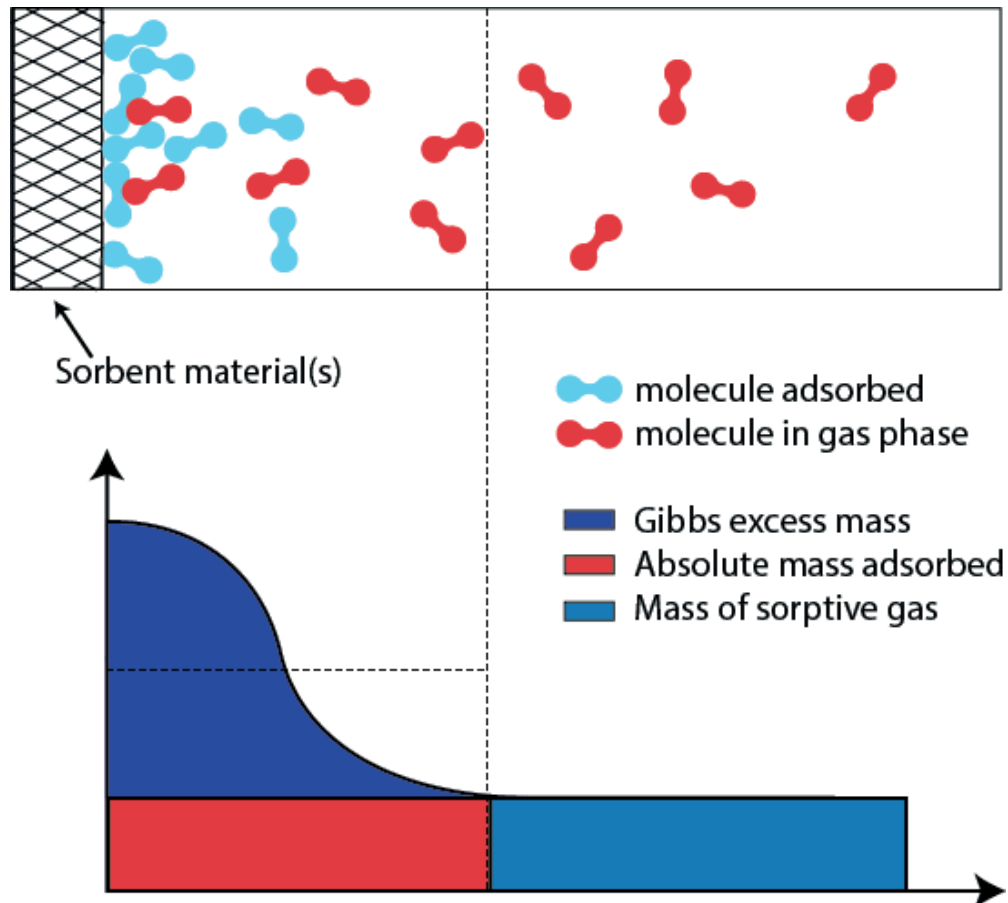


**Figure 4** Calculated hydrogen adsorption potential for slit shaped pores of different width.

Although adsorption instruments vary in technique and type, they all measure the same quantity called Gibbs excess adsorption ( $N_{ex}$ ) and is defined as follows[11].

*“The system of interest is a one-component gas in a volume  $V$  in the absence and in the presence of an adsorbing surface of area  $a$ . In both cases the gas has the same temperature  $T$  and pressure  $p$ . If  $N$  is the average number of molecules in the system with solid present and if  $N_0$  is the average number with solid absent, then the number of adsorbed molecules, by Gibbs' surface excess definition, is  $N - N_0$ .”*

The concept can be explained by a simple example sketched in Figure 5.



**Figure 5** Sorption system in a box of total volume ( $V$ ) including a certain mass of sorptive gas ( $m_{\text{system}}$ ) part of it being adsorbed on the surface of the adsorbent. The adsorbate having the absolute mass ( $m_a$ ) and the Gibbs surface excess mass ( $m_{g,\text{Gibbs}}$ ) (after Keller, 2005).

The system consists of a dense, square sorbent material of mass ( $m_s$ ) and volume ( $V_s$ ) with only one side exposed to the gas. Thus, the local gas density ( $\rho$ ) only depends upon coordinate  $x$ , directed perpendicular to the plane surface of the adsorbent, and increases towards the surface due to attractive forces from the adsorbent. The boundary between adsorbed gas and non-adsorbed gas is diffuse because molecules from the liquid phase may change their status of being adsorbed or desorbed between two molecular collisions. To overcome this problem, Gibbs proposed a reference system which occupies the same volume as the real system so that:

$$V = V_s + V_a + V_g = V_{s,\text{Gibbs}} + V_{g,\text{Gibbs}} \quad (1.1.1)$$





Here, subscript a stands for adsorbed layer and g respectively for the gas phase. In the Gibbs picture the concentration of the adsorptive gas remains constant in  $V_{g,Gibbs}$  and extends to the adsorbent's surface ( $V_{s,Gibbs} = V_s + V_a$ ). The mass in the gas phase is therefore given by

$$m_{g,Gibbs} = \rho_g(V - V_{s,Gibbs}) \quad (1.1.2)$$

From the mass balance of the adsorptive gas

$$m_{system} = m_{a,Gibbs} + m_{g,Gibbs} \quad (1.1.3)$$

it follows

$$m_{a,Gibbs} = m_{system} - m_{g,Gibbs} \quad (1.1.4)$$

Now consider the same system with the same temperature T and pressure p, but without the attractive force from the adsorbent's surface.

$$m_{system} = \rho_g^*(V - V_s) \quad (1.1.5)$$

Combining 1.1.2, 1.1.4 and 1.1.5  $N_{ex}$  becomes

$$N_{ex} = (\rho_g - \rho_g^*)(V - V_s) \quad (1.1.6)$$

since  $V_{s,Gibbs}$  is set to  $V_s$  in Gibbs' approach.