# GAS ADSORPTION ON CARBON NANOHORN AGGREGATES

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## Abstract

We evaluate a simple model of adsorption to predict the possible adsorbed phases of gases on a triangular array of parallel tubes as a function of the distance between the tubes and the external pressure. Based on these results, we propose a model for the interstitial spaces in a nanohorn aggregate that combines two regions with different separations between the tubes. We perform Grand Canonical Monte Carlo simulations for particular choices of the aggregates' geometry. Adsorption isotherms are presented for the cases of Ne and $CF_4$. Comparison with experimental results allows us to obtain information on the structure of the aggregates that is then use to predict the adsorption behavior of other gases.

## Introduction

Aggregates of single-walled nanohorns were first identified as new carbon structures in 1999 [Iijima, 1999]. A nanohorn is a single-walled hollow tube with a cone at one end. The tubes length range from 30-50 nm with diameters around 2 nm. Unlike nanotubes, which cluster together parallel to each other, nanohorns form spherical aggregates [Iijima, 1999; Murata, 2000; Murata, 2001; Yamaguchi, 2004]. Nanohorn aggregates present two groups of pores: inter-nanohorn pores, i.e. the interstitial spaces between individual nanohorns; and, intra-nanohorn pores, i.e., the hollow interior spaces of the individual nanohorns (access to this latter set of pores requires subjecting the nanohorns to an opening treatment).

The quasi-radial arrangement of the nanohorns (where the wall-to-wall distance of the tubes increases gradually from the center to the outer parts of the aggregate) suggests that most of the interstitial spaces between the nanohorns (which may provide the highest binding in the aggregate) should be accessible to adsorbates. This is quite different from what occurs in bundles of SWNTs, where the interstitial channels in the cylindrical bundles are generally much more difficult to gain access to. In addition, it is expected that the kinetics of the gas toward the interior of the aggregate will be facilitated in the radial arrangement of nanohorns, since the gases would access the pores through relatively wide entrances and would move to reach the narrower and higher binding energy regions in the interior of the aggregate. While the adsorption inside individual nanohorns can be modeled by starting with a cylindrical pore terminated with a cone cap with relatively well-known parameters, the interstitial pores between individual nanohorns in an aggregate are more difficult to model. Originally, X-ray diffraction measurements suggested that the distance between adjacent nanohorns in an aggregate was close to 0.4 nm [Bandow, 2000]. However, subsequent $N_2$ adsorption measurements and computer simulation studies were used to estimate this distance at ~ 0.7 nm [Ohba, 2005].

Adsorption processes on carbon nanohorns have already demonstrated some of their potential for practical applications, including methane storage, drug delivery systems, catalyst support and sieving. However, most of the fundamental adsorption research conducted on nanohorns has been quite limited in scope. Basic adsorption characteristics such as a thorough identification of the different groups of adsorption sites as well as values for the heats of adsorption for different species have been relatively less explored. Since the aggregates posses a relatively large degree of inhomogeneity, adsorption studies of gases with markedly different sizes are crucial to better identify and characterize all adsorption sites. Different gases are expected to access adsorption spaces of different size and energies, and then, comparing their adsorption isotherms would provide information about the structure of the aggregates. Therefore, in this work, we focus on a comparative study of the adsorption behavior of $CF_4$ and Ne on the interstitial spaces of as-produced nanohorn aggregates.

We first explore the presence of different adsorbed phases between parallel tubes in a triangular array by means of a simple model of adsorption. Then, we use those results to formulate a first approximation of the interstitial pore where we consider two regions between parallel tubes characterized by two different separations between the tubes. We use Grand Canonical Monte simulations of adsorption for both gases between tubes separated by the same two distances to generate the adsorption isotherms. We explain the presence of two plateaus observed in the experimental isotherms based on this model of the structure of the aggregate.

# Adsorption in a Triangular Array of Parallel Tubes: Simple Model

The starting point of this thermodynamic model of adsorption is to consider the total free energy of the system *F* as a sum of bulk energy, surface energy, and gas-substrate interaction terms. The next step is to compare the grand free energy $F - \mu N$ ($\mu$ being the chemical potential) of different hypothetical phases to determine which is realized at different thermodynamic conditions. The results are presented in the form of phase diagrams, using parameters relevant to the system considered. This approach has yielded results in agreement with much more sophisticated techniques, and due to its simplicity it certainly represents a sensible first step in getting initial insights [Gatica, 1999; Gatica, 2002]. It also has the advantage of allowing a rapid exploration of the dependence of the adsorption behavior on the geometric parameters of the substrate.

In the triangular arrangement, there are two possible phases that can be formed depending on the distance between the tubes. For small separations between the tubes, a condensed phase will occur, where the interior of the space would be completely filled with gas (Fig. 1). At larger separations, a film can occur around the tubes (Fig. 2) at the lowest pressures. By further increasing of the pressure, a condensed phase will eventually form where the interior is filled as well.
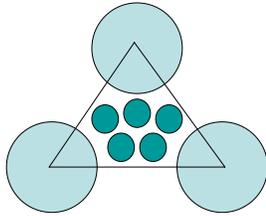


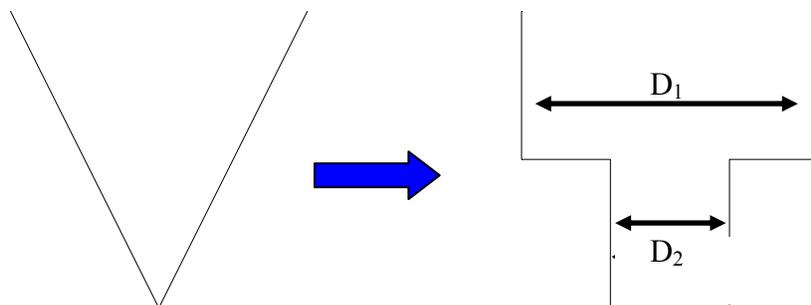**Figure 1.** Schematic depiction of the condensed phase between the tubes.
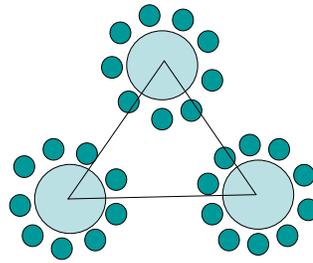


**Figure 2.** Schematic depiction of the film phase between the tubes.

Figure 3 shows the phase diagram for Ne at a temperature T=25 K. For a particular value of the center-to-center distance d between the tubes, a step in the isotherm would indicate the presence of a phase transition as the chemical potential increases. If the tubes are too close, only a transition to the condensed phase is possible while for tubes farther apart a film phase can exist before the condensed phase forms.
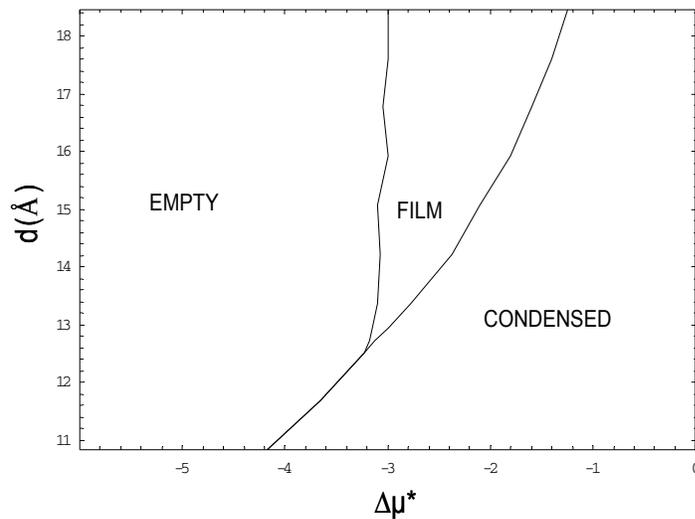


**Figure 3.** Phase diagram for Ne at T=25 K.

Experimental isotherms obtained by different research groups for small gases like Ne as well as for larger gases like $N_2$ or $CH_4$ show the presence of two steps. Since the size of the adsorbates is so different, the results from the simple parallel tubes model suggest that those two steps cannot be explained assuming that the interstitial spaces are characterized by a single pore diameter. In fact, if we take into account that the tubes are closer to each other near the center of the aggregate and gradually diverge toward its periphery, it is expected that the molecules will completely fill the smallest pore space in the interior of the aggregate before being adsorbed on the walls of the individual nanohorns, where they are much further apart. Therefore, we propose a model of the interstitial space where there are two regions between parallel tubes characterized by two different separations between the tubes.



**Figure 4.** Schematic depiction of the proposed structure of the interstitial pores to reproduce the effects of the wedge-shaped space.

## Modeling the quasi-conical interstitial pores: Grand Canonical Monte Carlo simulations

Adsorption isotherms obtained by Grand Canonical Monte Carlo simulations (see for example Calbi, 2001) are shown in Figure 5. Due to their different size, $CF_4$ and Ne form different kind of adsorbed phases in each region, but both set of isotherms can be reasonable well described with the same set of separations between the tubes; this internal consistency between the sets of data is an indication of the correctness of our model. By running several simulations with different radii we were able to determine that the center-to-center distances that most closely match the experimental results were 27 Å and 34 Å.
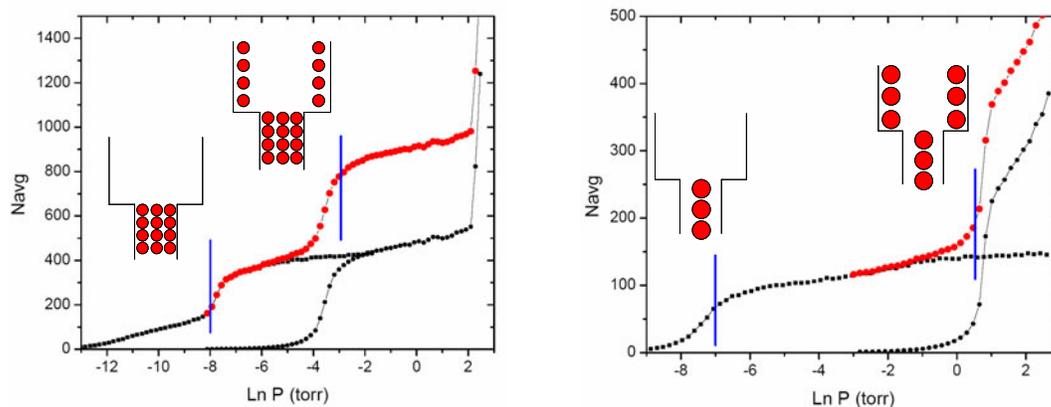


**Figure 5.** Simulated adsorption isotherms of Ne (left panel, 25 K) and $CF_4$ (right panel, 125 K). The total isotherm (top curve) is the sum of individual isotherms with the distance between the tubes set to 2.7 nm (left curve) and 3.4 nm (right curve). The diameter of the nanohorns is 2 nm.

# Conclusions

We propose a model for the interstitial pores in a nanohorn aggregate that involves two regions characterized by different distances between parallel nanohorns. By comparing with preliminary experimental data, we are able to determine the pair of characteristic distances that reproduces the experimental results for gases of very different size. Although the testing of this approach is currently at a preliminary stage, the results are promising and they illustrate the importance of modeling in interpreting the experimental results, especially when the structure of the substrate is not completely known. The immediate next step is to obtain the isosteric heats of adsorption that, when compared to experimental values, should provide additional support for the above picture.

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