COMPUTER SIMULATIONS OF NITROGEN ADSORPTION IN CARBON NANOTUBE ARRAYS

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Introduction

Since the discovery of carbon nanotubes, numerous studies have been conducted on the synthesis, treatment and physical properties of these novel materials. Also, some theoretical, experimental and molecular simulation studies on the adsorption of carbon nanotubes have been published [1-3]. Although some studies show that carbon nanotubes might be good adsorbents, nitrogen adsorption experiments on carbon nanotubes published so far show very low surface areas, ranging from only 15 to 250 m²/g [2,4]. These values are much lower than BET surface areas of commercially available activated carbons (~1000 m²/g). On the other hand, since most molecular simulations have been carried out on isolated carbon nanotubes, it is difficult to compare the simulations and experimental results. In this sense, adsorption in carbon nanotubes requires much more simulation and experimental work to be done. Bearing in mind that carbon nanotubes are often found in bundles or ropes and that they will be in some form of assembly in practical applications, we carried out simulation studies of nitrogen adsorption at 77 K in square and hexagonal arrays of single wall carbon nanotubes (SWCNT) with varying tube diameters and tube separations. Both closed and open nanotube arrays were studied.

Models and Simulations

In our models, SWCNT of diameter D are aligned uni-directionally along the tube axes in either square or hexagonal arrays. The separation between nanotubes, G, is measured as the internuclear distance between adjacent carbon atoms on opposite tube walls. Grand canonical Monte Carlo molecular simulations were employed and a Lennard-Jones (LJ) 12:6 potential is used to represent the interaction between nitrogen molecules. The interaction between adsorbate molecules and the tube is represented by a LJ 12:6 potential integrated over the tube wall [3]. The LJ energy and length parameters used are: σ_{ff} = 3.572 Å, σ_{sf} = 3.494 Å, ε_{ff} / k_B = 93.98 K and ε_{sf} / k_B = 53.52 K, where k_B is Boltzmann's constant.

Results and Discussion

Figures 1-3 show simulated isotherms of nitrogen at 77 K adsorbed in square arrays of closed SWCNT as a function of tube diameter, D, with three different tube separations, G. For a separation of 4 Å (Figure 1), that is the tubes are nearly contacting each other, all isotherms of tubes with diameters up to 30 Å are of type I shape, indicating a microporous behaviour. This is a result of the strongly enhanced interaction potentials in the interstices among the tubes. As tube diameter increases, the interstitial space available to the adsorptive increases, resulting in an increase in the amount adsorbed. Single point estimation of the BET surface areas from the isotherms ranges from ~300 m² g⁻¹ for the smallest tube to ~1000 m² g⁻¹ for the tube with a diameter of 30 Å.

Upon increase of tube separations, the amount adsorbed increases dramatically, as can be seen from the Figures. This is simply because more space is available for the adsorbate. In addition, the shapes of the isotherms also change systematically. A monolayer plateau and a condensation step become clearer as tube
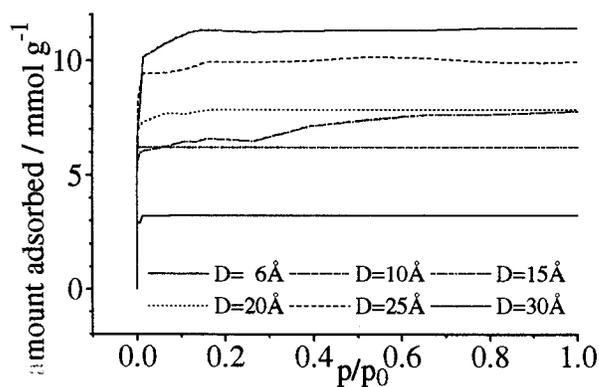

Figure 1. Isotherms for square arrays of closed SWCNT with G=4 Å and varying tube diameters, D.

separation increases. When tube separation reaches 20 Å, the isotherms can be regarded as Type IV, indicating both monolayer completion and condensation in the pore space. For G=25 Å, the monolayer plateau covers a wide

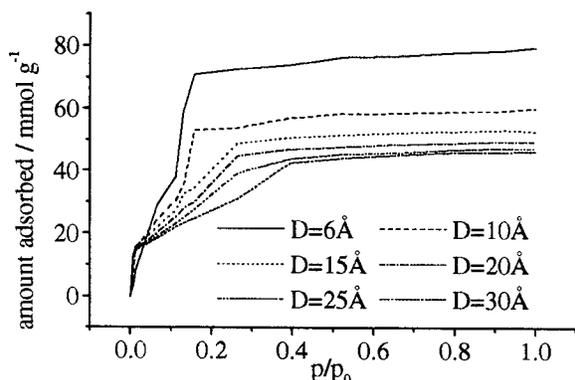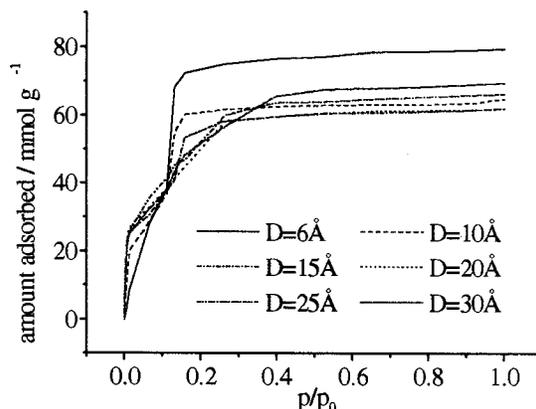**Figure 2.** Isotherms for square arrays of closed SWCNT with G=15 Å and varying tube diameters, D.

Figure 4. Isotherms for square arrays of open SWCNT with G=15 Å and varying tube diameters, D.
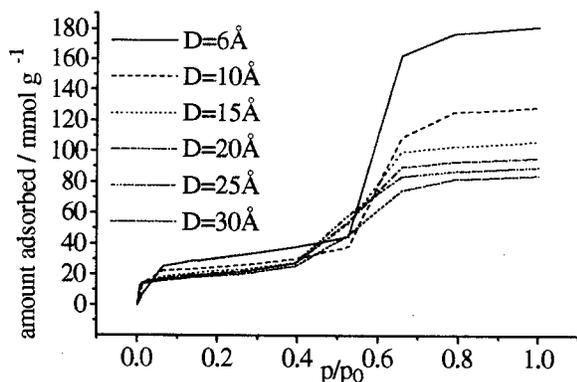

Figure 3. Isotherms for square arrays of closed SWCNT arrays with G=25 Å and varying tube diameters, D.

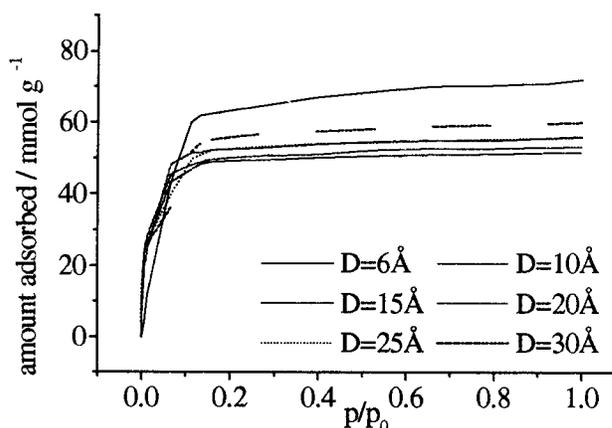**Figure 5.** Isotherms for hexagonal arrays of open SWCNT with G=15 Å and varying tube diameters, D.

range of relative pressures, Figure 3.

The isotherms for open tube arrays have similar shapes as those for closed tube arrays, c.f., Figures 2, 4 for G=15 Å. As expected, the amount adsorbed at the knee here is higher than in the case of closed tubes, resulting in higher specific surface areas. At higher pressures, the amount adsorbed here is generally higher than closed tube arrays. However, the difference is not marked, indicating at in such SWCNT arrays interstitial adsorption plays a more important role than endohedral adsorption. At very small G adsorption is less important than endohedral adsorption.

In hexagonal arrays, interstitial space is less than in square arrays, resulting in lower adsorbed amount and the arrays are filled at lower pressures, c.f., Figures 4, 5.

Conclusions

Adsorption in carbon nanotube arrays depends strongly on their configuration and packing. The

simulation results presented here may be used to compare with future experimental adsorption experiments and to characterise nanotube materials.

References

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