# COMPLETE CHARACTERIZATION OF STRUCTURAL HETEROGENEITY OF SINGLE WALLED CARBON NANOTUBES: NEW T-PLOT METHOD

*Sandeep Agnihotri*

Environmental Engineering, in the Department of Civil & Environmental Engineering, University of Tennessee, Knoxville, 37996-2010

## Introduction

We have developed a microporosity and surface area estimation method that is specific to single-walled carbon nanotubes (SWNTs). Typically, micropore volume of adsorbents can be determined by the t-plot method, where the statistical thickness, *t*, of adsorbed layer is a function of the adsorbed amount, and is estimated by several equations such as de Boer equation, Halsey equation and Carbon Black equation. The t-plot method is one of the most common and versatile method. The estimated micropore volume is often specific to a model and to the segment of adsorption isotherm that is fitted to that model. SWNTs are essentially microporous carbons but the applicability of traditional models to carbon nanotubes needs evaluation. We have developed a technique that compares experimental $N_2$ adsorption isotherm (77 K) of a sample with grand canonical Monte Carlo (GCMC) simulation isotherms of $N_2$ on the external surface of SWNT bundles ($10^{-6} < P/P_o < 0.99$). In this method, we plot the total experimental adsorption capacity vs. simulated external adsorption capacity from SWNT bundles. The plot is more or less a straight line for adsorption at $P/P_o \geq 10^{-3}$. The slope and intercept of the linear asymptote of the curve are interpreted as the external surface area of the bundles and the available micropore volume, respectively. We are also able to incorporate adsorption from impurities by modeling impurities as planar carbons and adding it to the total non-endohedral contributions. The main advantages of our method is that it is specific to SWNTs and, unlike other methods, it includes the entire experimental adsorption isotherm ($10^{-6} < P/P_o < 0.99$) in analysis, thus minimizing any experimental errors related to selecting an appropriate segment of an experimental isotherm to fit the data.

## Experiments

The study was performed on a commercially available 95-98 wt% SWNT sample produced by electric arc method (designated as EA95). The samples were analyzed by Raman scattering ($\lambda$ = 785 nm, Table 1). Samples were also characterized by $N_2$ adsorption (77 K, $10^{-6} < P/P_o < 0.99$).

**Table 1. Diameter distribution of SWNTs from Raman**

| Sample | wt% | | Diameter (Å) | Relative amount |
|---|---|---|---|---|
| | SWNTs | Impurities | | |
| EA95 | 95 - 98 | 3 - 5 | 11.5 | 1.0 |
| | | | 14.0 | 2.3 |
| | | | 15.2 | 3.5 |

## Description of Method

*1. Calculation of Statistical Thickness by $N_2$ (77 K) GCMC simulations.* Our method requires estimation of $N_2$ adsorption on the external surface of the SWNT bundles. This was performed by GCMC simulation (Fig. 1).



**Fig.1.** (a) Cross section of the unit simulation box for GCMC study of $N_2$ adsorption on the external groove sites and external surface of SWNT bundles at 77 K. (b) We define the external surface area of a bundle as the area of the plane boundaries of the prism with vertices on the center of the outermost shell of nanotubes (solid line). This is an unambiguous definition of external surface that is independent of sorbate size. It can be converted to that represented by the dashed line using the conversion formula $S'_p = S_p(\pi/2 - \theta)/\cos\theta$, where $\cos\theta = (D + \Delta_s)/(D + \sigma_{sf})$, $D$ is the tube diameter, $\Delta_s = 3.4$ Å is the intertube distance, and $\sigma_{sf}$ is the collision diameter for sorbate-carbon interaction.

Each nanotube was approximated as a smooth structureless nanocylinder at the temperature of interest. The intertube distance for all simulation is kept fixed at 3.4 Å to mimic SWNTs adhering to each other via van der Waals forces forming bundles. Each pseudoatom of the adsorbate molecule is treated as a structureless spherical particle which interacts via dispersive forces only. The interaction between adsorbate molecules is modeled by the 12-6 Lennard-Jones (LJ) potential. The cross terms are obtained using the standard Lorenz-Berthelot combination rules. For modeling of $N_2$ adsorption at 77 K, the well depths $\varepsilon_{C-C}/k_B$ and $\varepsilon_{N2-N2}/k_B$ used in calculations are 28.0 K and 100.4 K, respectively, and the collision diameters $\sigma_{C-C}$ and $\sigma_{N2-N2}$ are 3.4 Å and 3.69 Å, respectively. The GCMC simulation is carried out using established procedures. Simulations revealed that the peripheral grooves on nanotube bundles play an important role in adsorption on the surface of nanotubes (Fig. 2.).



**Fig.2.** Adsorption on $D$ = 9.0 Å (left) and $D$ = 15.2 Å (right)

Adsorption was observed at pressures as low as $10^{-6}$ P/P$_o$. At such pressures, some N$_2$ molecules were noticed to adsorb on the external grooves sites. Adsorption continued on the grooves until they were saturated at about $10^{-4}$ P/P$_o$. Increasing the vapor concentration resulted in adsorption on the curved surface of the nanotubes. At $10^{-3}$ P/P$_o$, partial coverage of the external surface was observed. Further increase in vapor concentration until $10^{-2}$ P/P$_o$ resulted in complete monolayer formation following which adsorption proceeded rapidly with increasing P/P$_o$. It was also observed that the trends in external adsorption were independent of the nanotube D. Adsorption on an array of 15.2 Å diameter nanotubes proceeded in more or less the same fashion as that on 9.0 Å wide nanotube array, which showed that nanotube size has little or no effect on the total external adsorption capacity (Fig. 3).



**Fig. 3.** Exohedral N$_2$ adsorption isotherms at 77 K calculated for homogenous bundles of nanotubes sizes typically found in SWNT samples.

*2. Estimating Micropore Volume and External Surface Area from Experimental N$_2$ Isotherm and GCMC Statistical Thickness.* The statistical thickness calculated by simulations was then plotted against the adsorption capacity in a manner similar to the V-T plot. The external surface area of > 95 wt% SWNT sample was determined (Fig. 4). The plot is interpreted to comprise of two regions: the first region shows a steep rise and the second region that nearly follows a straight line. The first region of the curve indicates that the experimental adsorption capacity surpassed the simulated values, which means that the internal adsorption in the sample was much higher than the adsorption on its external surface. The second region of the curve implies that the experimental adsorption capacity was linearly proportional to the simulated external adsorption capacity or, in other words, majority of the adsorption in this pressure range occurred on the external surface of the bundles. The intercept of the straight line through the linear part of the curve provides the micropore volume of the sample because the amount adsorbed at zero surface loading is adsorbed entirely inside the pores. Additionally, the slope of the second region of the curve, thus,

represents the total external surface area of nanotubes in the sample. Furthermore, the relative pressure at the point of inflexion in the curve (i.e., meeting point of the two regions of the curve) is indicative of the maximum pressure above which the internal volume of nanotubes will be filled. We found that the external surface area of the sample was 160 m$^2$/g and the micropore volume was 0.16 cm$^3$/g.



**Fig. 4.** Total experimental adsorption capacity (Y axis) vs. surface adsorption capacity from Fig. 3 averaged according to the Relative Amount in Table 1 (X axis) for 95 wt% pure SWNT sample. The intercept and slope of the straight line represents micropore volume and total external surface area of nanotubes.

**Table 2. Comparison with traditional methods**

|  | Traditional Methods | | | Our Method |
|---|---|---|---|---|
|  | De Boer | CB | Halsey |  |
| Micropore Volume (cm$^3$/g) | **0.16** | **0.15** | 0.10 | **0.16** |
| External Area (m$^2$/g) | **160** | **156** | 210 | **160** |

**Conclusions**

We are reporting a method for estimating the microporosity and external surface area of single-walled carbon nanotubes (SWNTs). The method is similar to the V-T plot approach; however, here the statistical thickness, t is estimated by GCMC simulations of N$_2$ at 77 K for an external corrugated surface of nanotubes. The plot is more or less a straight line for adsorption at P/P$_o$ $\geq$ $10^{-3}$. The slope and intercept of the linear asymptote of the curve are interpreted as the external surface area of the bundles and the available micropore volume, respectively. The results are comparable to those from traditional methods (Table 2).