

MOLECULAR SIMULATION OF CAPILLARY CONDENSATION OF N₂ ON MULTIWALL CARBON NANOTUBES

T. Suzuki, S. Inoue, K. Kaneko, and W.A. Steele †

Graduate School of Natural Science and Technology, Chiba University 1-

33 Yayoi, Inage, Chiba 263-8522 Japan

Takaomi@pchem2.s.chiba-u.ac.jp

† Department of Chemistry, 152 Davey laboratory, Pennsylvania State University, University Park, PA

16802 USA

1. Introduction

Molecular adsorption in mesopores has been described in terms of the classical capillary condensation theory. However, the fact that adsorption hysteresis of N₂ adsorption isotherms of mesoporous silica material depends on the pore width has stimulated a fundamental question on capillary condensation. The molecular system even in mesopores needs fundamental research from the various approaches. Consequently, a molecular adsorption study on carbon nanotubes could shed light on molecular systems in small confined spaces, even though carbon nanotube samples were not perfect and it is not easy to extract adsorption only in pores. Also molecular simulations can be precisely applied to molecular adsorption on the ideal carbon nanotube owing to the simpler potential calculation than for mesoporous silica.

2. Experimental

Multiwall carbon nanotube powder (Hyperion Catalysis Int. Co.) was used without further purification. The carbon nanotube crystals were examined with a high-resolution transmission electron microscope operated at 400 kV after ultrasonically suspending in CCl₄ and drying. The N₂ adsorption isotherm at 77 K was gravimetrically

determined using a computer-aided apparatus.

3. Simulation

The intermolecular interaction between N₂ molecules is approximated by the one-center Lennard-Jones potential. The interaction potential $u_{X-s}(R)$ of an N₂ molecule with a single graphite slab is described by the integration of the each adsorbate molecule-carbon atom potentials.

$$u_{X-s} = 4\epsilon_{X-C}\rho_C \sum_n \int_{-\infty}^{\infty} dz \int_0^{\pi} a_n d\phi \left\{ \left(\frac{\sigma_{X-C}}{r_{X-s}} \right)^{12} - \left(\frac{\sigma_{X-C}}{r_{X-s}} \right)^6 \right\}$$

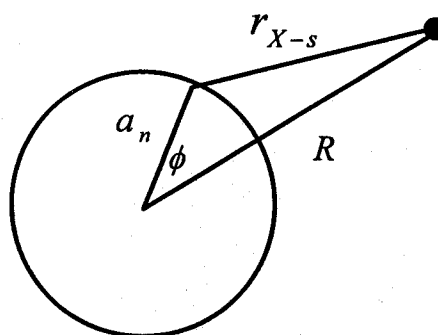


Fig. 1

This integral was calculated as,

$$u_{X-s} = 4\rho_C\epsilon_{X-C} \left\{ \sigma_{X-C}^{12} I_6 - \sigma_{X-C}^6 I_3 \right\}$$

where

$$I_m = \frac{2\pi c_m}{a_n^{2p-1}} F(p, p, 1; \beta^2)$$

for inside and

$$I_m = \frac{2\pi c_m a_n}{R^{2p}} F(p, p, 1; \delta^2)$$

for outside. F is the hyper geometric function.

The GCMC calculation of the adsorption isotherm at 77K was carried out for the 7-layered concentric graphitic cylinder model for inner and external surface, independently.

4. Results and discussion

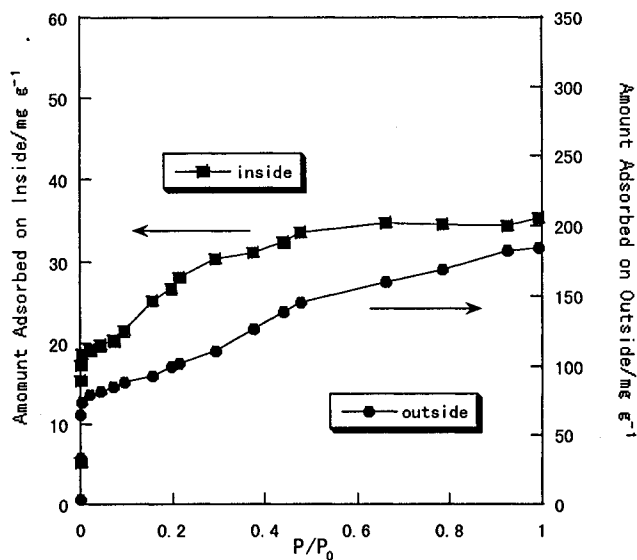


Fig.2

The calculated adsorption isotherms of N_2 for inner and external surface of carbon nanotube are shown in Fig. 2. The diameters of inner and external surfaces are 2.30nm and 7.08nm, respectively. A steep rise at low pressure region was observed for both adsorption isotherms, which correspond to the formation of the monolayer of adsorbed molecules. The snapshot for the adsorption on inner surface at $P/P_0=0.004$ is shown in Fig. 3. The gradual increase of the adsorption at around $P/P_0=0.4$ region correspond to the capillary condensation, and the snapshot of the adsorption at $P/P_0=0.37$ for inner surface is shown in Fig.4. The simulated adsorption isotherms have good agreement with experimental

isotherm only at low pressure region. Especially, in the experimental isotherm a steep rise at the region of $P/P_0 > 0.6$ which correspond to the condensation of N_2 molecules in the space of inter nanotube was observed. We are going to report the effect of the adsorption in the inter nanotube space using improved simulation program. Also going to discuss about the pore size dependence of the capillary condensation on the inner surface of the carbon nanotube by computer simulation.

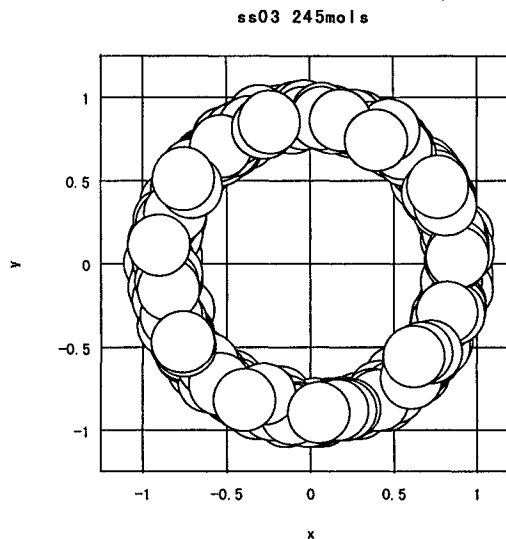


Fig.3

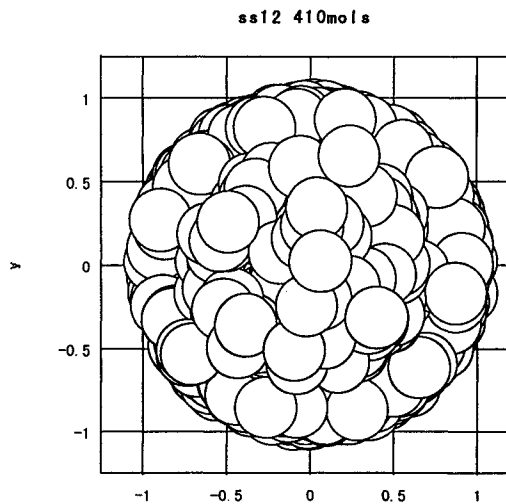


Fig. 4