Adsorption of ^{4}He on carbon nanotube bundles

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Abstract

We have measured adsorption isotherms of helium on bundles of Single Walled Carbon Nanotubes (SWCNs) in the temperature range from 2 to 14 Kelvin. The isotherms and resulting isosteric heat suggest the bundles have sites with differing binding energy for adsorption on the first layer. The results are consistent with the standard interpretation that the bundles have high binding energy sites in either the interstitial channels or the grooves where two tubes meet on the external surface, and a lower energy, graphene like binding to the rest of the external surface. We present a comparison with results of experimental and theoretical studies on the same system.

Key words: nanotubes; physisorption; helium

1. Introduction

One of many interesting possibilities presented by SWCNs is that adsorbates may behave one dimensionally (1d) under some conditions[1]. Many calculations for 1d ^{4}He have been made[2–4]. From a strictly geometric point of view there are four distinct site types on a SWCN bundle (Fig. 1). In our samples all of the tubes are closed, so the tube interior sites (1) are not accessible. The accessibility of the interstitial sites (2) is a matter of controversy[5]. The groove sites (3) are clearly accessible and are at least partially responsible for the high binding energies seen in experiments. The outer suface sites (4) should have binding energies similar to, but smaller than that for graphite[1]. Previous experiments by Teizer *et al.* and Khang *et al.*[6,7] have deduced the binding energy of ^{4}He on SWCNs by fitting programmed thermal desorption data. the goal of our experiments is to obtain very accurate equilibrium adsorption isotherm data to find directly the isosteric heat of adsorption and to extend the measurements to multilayers at lower T.

Adsorption isotherms measure the equilibrium pressure after adsorption of known amounts of adsorbate at constant temperature[5,8]. We used a glass cell, which limited the upper pressure range to around one atmosphere. The lower pressure range was set by our Baratron pressure gauges, which have a resolution of 10^{-4} torr. The cell contained 50 mg of SWCN bundles, made and characterised at Montpelier[9]. The sample consists of bundles with a mean number of 37 tubes with a mean diameter of 13.8 Å arranged in a hexagonal array

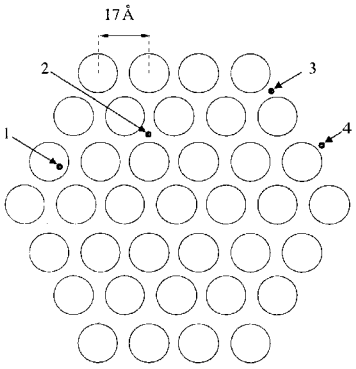

Fig. 1. Here is an idealized cartoon of a bundle of SWCNs, showing the geometry of the bundle itself, and the location of various adsorption sites: 1 - tube interior, 2 - interstitial channels, 3 - external grooves, 4 - outer surface.

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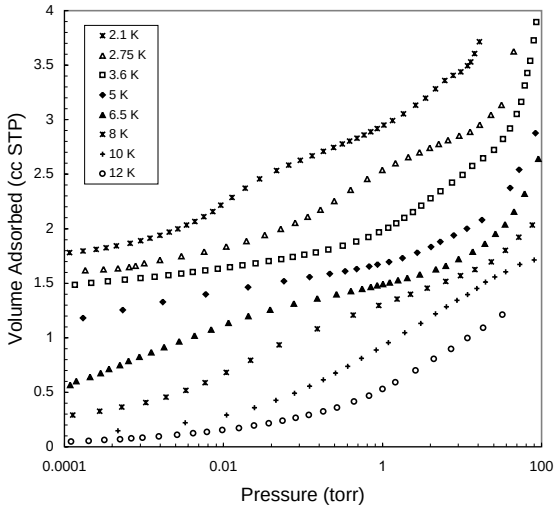

Fig. 2. A few of the isotherms. The large plateau at 1.5 cc is the completion of the first layer.

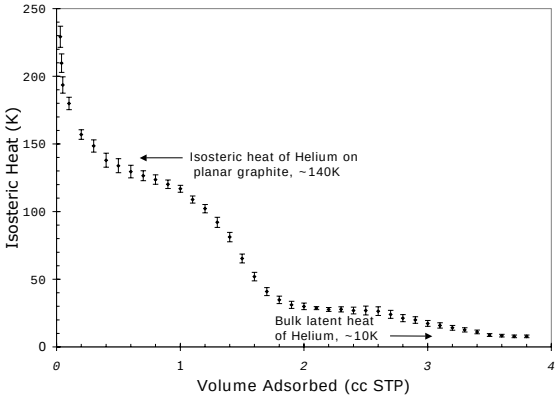

Fig. 3. The isosteric heat of adsorption as a function of film coverage.

with mean nearest neighbor spacing of 17 Å (Fig. 1). The sample is 80% by mass nanotubes, the rest being 5% catalyst and 15% amorphous carbon and graphite. The specific area for adsorption on the bundles is so large (~ 80 m^2 per gram) that we expect the signal from adsorption to any 'junk' in the cell to be small compared to adsorption on the bundles.

2. Results

Our isotherms are presented in Fig 2. The first layer is completed at 1.5 cc and is clearly not just one step. The first step occurs at much lower pressures than we can measure, and is not as distinct as it is with some other adsorbates[8]. This is reflected more clearly in the isosteric heat of adsorption ($Q_{\rm st}$)[10] (Fig. 3) which has a nice plateau for high coverage on the first layer, but strong binding at lower coverage. The strong dependence of $Q_{\rm st}$ on coverage at low coverages is in qualitative agreement with the desorption experiment of Teizer *et al.*[6,7]. Also the trend at $V_{\rm ads} \to 0$ is $Q_{\rm st} \to$ 240K, in rough quantitative agreement with that experiment and with the theoretical prediction of a 60% to 80% increase in the binding energy for adsorption on the grooves[5,11].

The $Q_{\rm st}$ plateau between 0.2 and 1 cc is slightly lower than that for planar graphite. We assume that this corresponds to adsorption on the outer surface of the bundle (Fig. 1) and that the curvature of the surface, as well as the absence of carbon layers below the first, is responsible for a small lowering of the binding energy in these sites compared to planar graphite. This result agrees well with measurements of H_2 and D_2 adsorption on similar SWCNs[8]. The two plateaus at still higher coverage correspond to further layering of the helium on the outer surface. The isosteric heat of the third layer approaches the latent heat of bulk helium and we see no further layering.

Our results are consistent with adorption first in the outer grooves of the bundles, with a high but strongly coverage dependent binding energy, then filling the rest of the outer surface with a graphene like binding energy, and finally layering on the outer surface.

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