

Adsorption and Phase Properties of Inert Gases on Suspended Carbon Nanotube Resonators

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Abstract

Carbon nanotubes offer a new regime for adsorption experiments in the one dimension limit, with much basis for comparison to pure two dimensional adsorption on graphitic surfaces. Using a single suspended carbon nanotube as a tuned resonator allows for sensitivity on the scale of single atoms. The relative shift in resonance frequency with the introduction of ^4He gas was used to detect adsorbate coverage of the tube. Data of the first successful adsorption isotherm of ^4He on a single suspended carbon nanotube is presented, as well as figures for the isosteric heat and a simple theoretical model for comparison. Marked difference between the two suggests that the quantum nature of helium must be taken into account in calculating the binding and zero point energies of ^4He on a single nanotube.

Introduction

Physical adsorption gives a probe of thermodynamic systems in reduced dimensions, where much new physics can be investigated. Extensive work has been done with two dimensional adsorbed layers (adlayers) on various substrates such as exfoliated graphite and MgO. These adlayers can exhibit phases distinct to 2D, such as a solid commensurate with the graphene lattice on graphite (one adsorbate per six carbon). On a single carbon nanotube, this 2D adlayer approaches the 1D limit, with imposed periodic boundary conditions around the nanoscale cylinder.

In the UW Nanodevice Lab, much work has been done with adsorption of heavy noble gases such as Krypton and Argon on single suspended carbon nanotubes, and a range of interesting phenomena found. These include the first order phase transition of Kr from 2D vapor to commensurate solid (Figure 1), occurring at higher pressures than on graphite (1).

Because physical adsorption rests on van der Waals dispersion forces for attraction, more highly polarizable gases are more easily adsorbed. The heavier noble gases are of this type, which we'll call "classical" adsorbates. For smaller adsorbates, the quantum mechanical na-

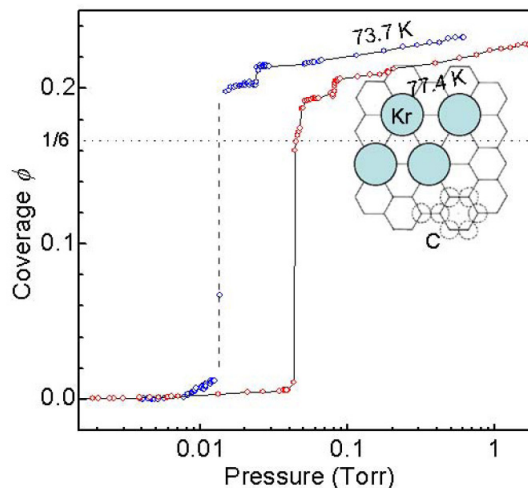


Figure 1: Jump in relative coverage of krypton on a nanotube showing first order phase transition to the commensurate solid phase at $\phi = 0.167$, 1 krypton per 6 carbon (1).

ture of the electronic interaction between the gas and substrate wave functions plays a more important role. Not surprisingly, we'll call this class "quantum" adsorbates, of which ^4He is an example. My work in the Nanodevice Lab this summer was to set up a new system for adsorption (4K helium cryocooler, gas handling system,

electronics setup, etc.), adapt an already existing program in *LabVIEW* called *Measureit* for that system, and then use that system to investigate adsorption of ^4He on a single nanotube.

Detection Mechanism

Single suspended carbon nanotubes are grown by chemical vapor deposition directly on chips with prefabricated electrodes and trenches to limit any defects that would be introduced by tampering with an already grown tube (2). For these volumetric adsorption isotherms, the mechanism of adsorbate detection is the shift in mechanical resonance frequency of the tube with changing density. We assume that the resonance frequency shifts are due to changing inertial properties of the nanotube (i.e. an adlayer), and not tensile ones.

We quantify this assumption by saying $f_{res} \propto \rho^{-1/2}$ at constant temperature, as would the resonance frequency of a classical string. Then, if ρ_0 is the density of carbon on the tube, $\Delta\rho$ is that of the adsorbed layer, and $f_0 = \lim_{\Delta\rho \rightarrow 0} f_{res}$,

$$\frac{f_{res}}{f_0} = \sqrt{\frac{\rho + \Delta\rho}{\rho}}. \quad (1)$$

Furthermore, if m_{carbon} and m_{ads} are the atomic masses of carbon and the adsorbate, respectively, we can say that the ratio of the number of adsorbed atoms to carbon atoms on the tube is given by

$$\phi = \frac{N_{ads}}{N_{carbon}} = \frac{m_{carbon}}{m_{ads}} \left[\left(\frac{f_0}{f_{res}} \right)^2 - 1 \right]. \quad (2)$$

In our setup, the tube is driven with an oscillating voltage $V_0 \cos(\omega t)$, which is amplitude modulated by the factor $1 + \cos(\delta\omega t)$, while the gate is held at a constant potential (Figure 2). The mechanical resonances of the nanotube appear as sharp resonances in frequency sweeps of the oscillating current, at the $\delta\omega$ frequency (Figure 3). The oscillating potential in the tube at frequency ω creates an electric field between the tube and the gate, which in turn drives the tube to oscillate at that frequency.

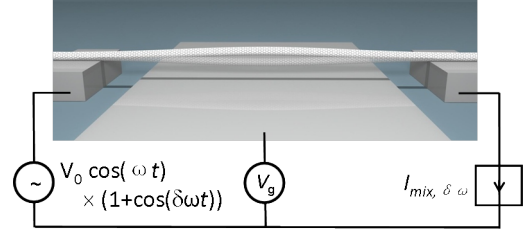


Figure 2: Depiction of the “nanoguitar,” showing driving signal and resulting mixing current at $\delta\omega$.

To see why this creates a peak in the electrical frequency response of the tube, we need to consider the dependence of the conductance, G , on frequency. When the tube is closer to the gate, more electrons (or holes, depending on the sign of the gate voltage) enter the conduction band, increasing the conductance of the tube. Therefore, when the tube’s oscillation amplitude peaks, so will the conductance. In this case, we find that for the current at the low AM frequency $\delta\omega$, $I^{\delta\omega} \propto z(\omega)$, where $z(\omega)$ is the amplitude response function of the nanotube (3).

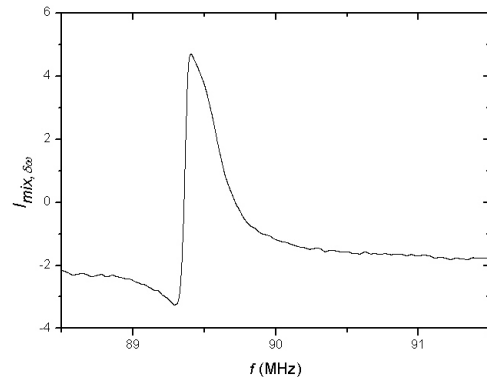
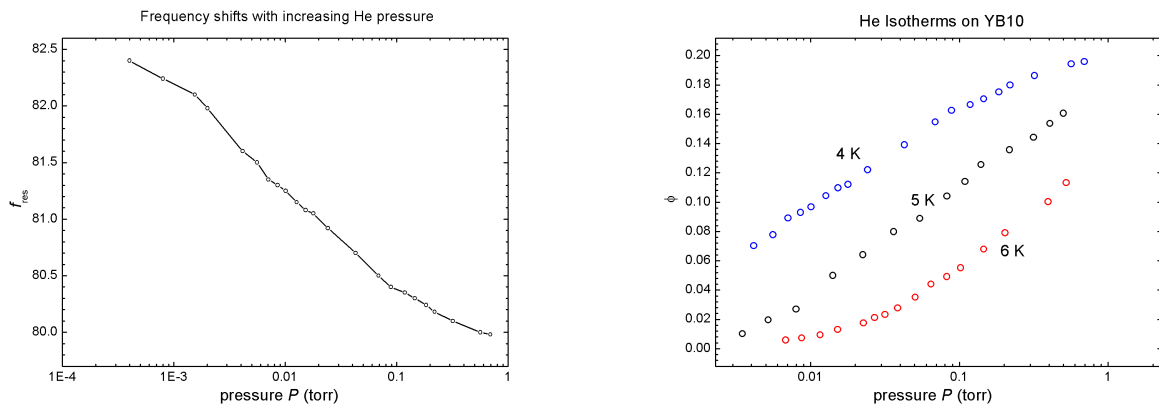


Figure 3: Frequency sweep plot of $f_{driving}$ vs. $I^{\delta\omega}$ showing example of mechanical resonance detection.

^4He adsorption

Adsorption of ^4He on any substrate is more difficult than the bigger noble gases due to its very low polarizability ($\alpha_{He} = 0.204 \text{ \AA}^3$ vs.



(a) Resonance frequency shift with pressure at 4 K.

(b) Isotherms at 4, 5, and 6 K on device YB10. Coverage vs. pressure plotted.

Figure 4: First isotherms of ^4He on a single suspended carbon nanotube.

$\alpha_{Xe} = 4.01 \text{ \AA}^3$). Since the induced dipole energy scales linearly with polarizability, this implies that adsorption of helium on a given surface must be done at much lower temperatures than for classical adsorbates like Kr and Ar, as only a small amount of thermal energy is needed to prevent helium from adsorbing to the substrate. Previous data collected from adsorption on carbon nanotube bundles suggests that most helium does not adsorb on the outer surfaces of single nanotubes (4).

We were able to perform isotherms at 4 K, 5 K, and 6 K, and found that there was indeed adsorption of helium on the nanotube (Figure 4). The maximum coverage we reached was a value of $\phi = 0.186$, while we would expect a full monolayer of helium to be above 0.2 coverage. We will likely need to go to lower temperatures to resolve coverages above the values shown in Figure 4b. Nevertheless, there is other important information to extract from the isotherm data.

An important experimental quantity in adsorption physics is the isosteric heat, which is the analogue in 2D of the 3D latent heat. Recall that latent heat is defined in the context of two phase coexistence in 3D, while the isosteric heat deals with the coexistence of the 3D gas and the

2D adsorbed layer. It is defined as

$$q_{st} = -k \frac{\partial \ln P}{\partial (1/T)} \Big|_{\phi}. \quad (3)$$

For further motivation of this definition, consider that in a system of two phase coexistence in 3D (to first approximation), $P = P_0 e^{-L/kT}$. Therefore, the latent heat L defines the slope of a line in $\ln P$ vs. $1/T$ space. This has been found to be the case experimentally with q_{st} along lines of constant coverage ϕ , as we found from our ^4He adsorption data (Figure 5). Our experimental value for the isosteric heat of adsorption of ^4He on a single nanotube was $q_{st}^{exp} = 42.9 \text{ K}$.

Simple Theoretical Model

The most commonly used potential for adsorption processes is the Lennard-Jones potential, which models the interaction between two identical atoms or molecules

$$V(r) = -4\epsilon \left[\left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right], \quad (4)$$

where ϵ and σ are measured parameters for distinct substances. To calculate this potential for the interaction between a single atom and a substrate, Equation 4 must be integrated over all

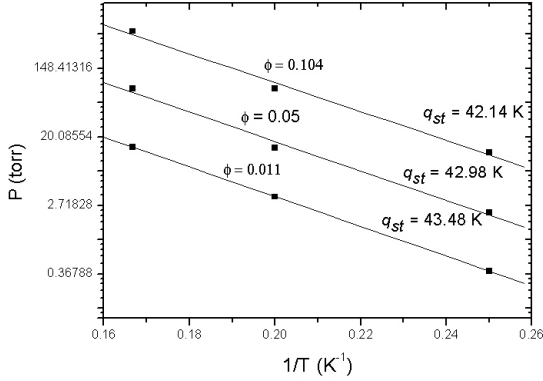


Figure 5: Measured isosteric heat values at various coverages.

of the atoms on the substrate (5). In this case, a crude model was used that approximated the nanotube as a 12 sided regular polygon, extended infinitely along the central axis so that there are 12 infinite “strips” of carbon (this model corresponds to what are called zig-zag nanotubes). Furthermore, the carbon is approximated to be continuous throughout the strips, while using the correct number density per unit area, $\rho_c = 0.384$ atoms/ \AA^2 (Figure 6). It should be noted that although this model is simple, it has been used to successfully calculate the binding energies of other noble gases in agreement with published theory papers. In this “strip” approximation, for a thickness $\frac{4.25}{\sqrt{3}} \text{\AA} dx$, the Lennard-Jones potential becomes

$$dV(z) = -4\epsilon_{gc}\rho_c \frac{4.25}{\sqrt{3}} \text{\AA} \times \left[\frac{\sigma_{gc}^6}{(x^2 + z^2)^3} - \frac{\sigma_{gc}^{12}}{(x^2 + z^2)^6} \right] dx, \quad (5)$$

where $\epsilon_{gc} = \sqrt{\epsilon_g \epsilon_c}$ and $\sigma_{gc} = (\sigma_g + \sigma_c)/2$ are the Lennard-Jones parameters for any gas (g) interacting with a carbon atom (c). The details of this integration are not shown here, but we will state that the attractive part of the potential goes as z^{-5} and the repulsive part as z^{-11} . The potential for a single strip was then evaluated at 12 discrete points on the tube (the vertices of the polygon) for a single helium atom at a distance

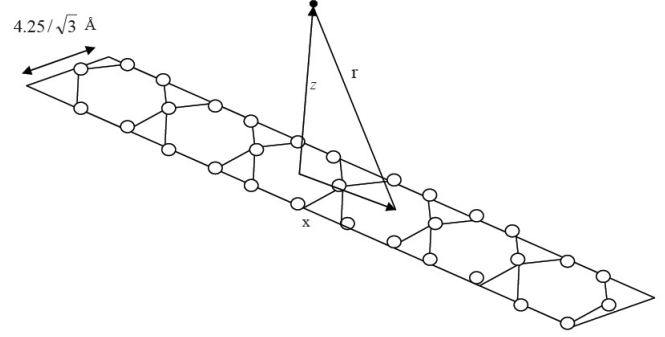


Figure 6: Depiction of the graphene strip. Carbon atoms are shown, though calculation assumes continuum mass distribution.

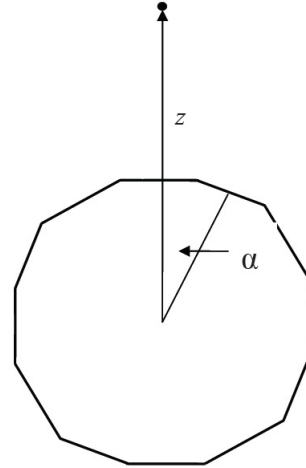


Figure 7: Cross section of the extended regular 12-gon. Integrated version of equation 5 evaluated at points corresponding to $\alpha = (2n-1)\pi/6$, where $n = 1$ is shown.

z from the center of the tube. This gives the potential shown in Figure 8, with a minimum at $E_{binding}/k_B = -131.4$ K.

In the limit of low coverage, ϕ , the repulsive dipole-dipole interaction between adsorbates is negligible, and the amount of free energy released for adsorption of a single atom (i.e. isosteric heat) is given by

$$\lim_{\phi \rightarrow 0} q_{st} = -E_{binding} + T\Delta S - E_{zp}, \quad (6)$$

where E_{zp} is the zero point energy for the bound atom, and the change in entropy upon adsorption, $T\Delta S$, is about kT (≈ 5 K in our case). For helium on graphite, typical values for E_{zp} are around 44 K. Using these values as well as our calculated value for $E_{binding}$, we obtain an approximate theoretical value for the isosteric heat of $q_{st}^{th} = 92.4$ K. This is more than a factor of two greater than our experimental value of 42.9 K.

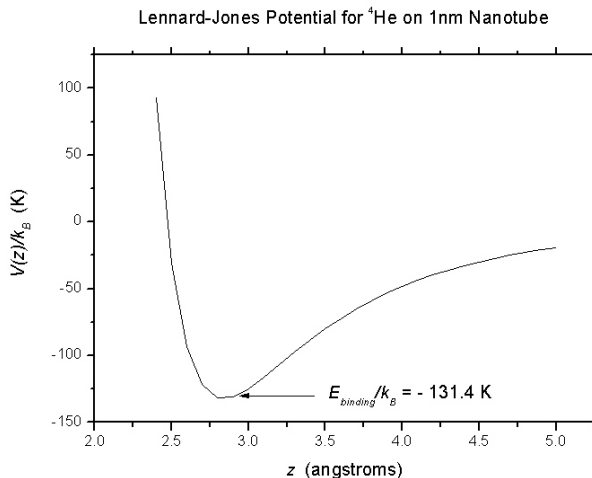


Figure 8: Calculated Lennard-Jones potential for ^4He on a 1 nm carbon nanotube.

The discrepancy between the calculated isosteric heat and the experimental value is not a big surprise. The fact that this model worked well with gases such as Kr and Ar furthers the distinction between “classical” and “quantum” adsorbates. Possible factors which were largely ignored in the classical calculation are the curvature effects of the tube. There is likely squeezing of the p_z orbitals of graphene on the inside of the tube, which would cause an extension of the electronic wave function outside of the tube. This could push the location of the potential minimum away from the tube, resulting in a shallower potential (as well as decreased E_{zp}). Experimentally, more data of helium adsorbed on tubes of different diameters is needed to get a firmer grasp on the effect of curvature in this nanoscale system.

References and Acknowledgments

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5. Model and calculations made by Professor Oscar E. Vilches.
6. My time at the University of Washington was funded by an REU grant from the NSF (PHY-0754333). The Nanodevice Lab I worked in is also funded by an NSF grant (DMR-0907690).
7. I would especially like to thank Professor David Cobden for hosting me at UW for the summer, and making my research experience rewarding and enjoyable.