Adsorption and Phase Properties of Inert Gases on Suspended Single Carbon Nanotubes

Ricky Roy

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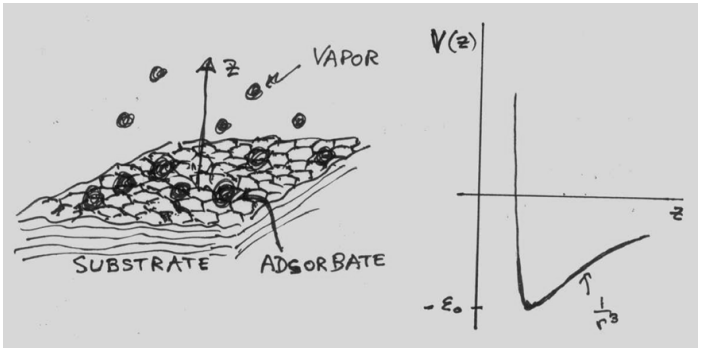
Physical Adsorption Basics

- 3D gas - substrate interactions
  - Van Der Waals dispersion energy always attractive
  - Repulsive forces at short distances due to wave function overlap

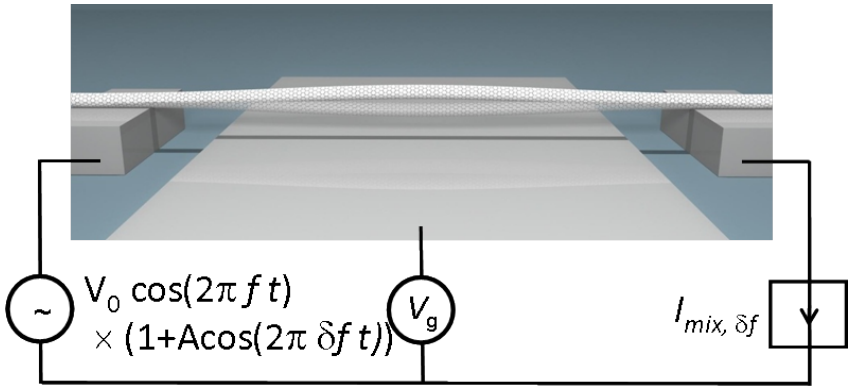


  - Lennard-Jones potential:

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

- 2D behavior (monolayers, phase transitions)
- Measurement methods
  - Calorimetry
  - Diffraction (neutrons, electrons, X-rays, etc.)
  - *Volumetric adsorption isotherms*
    - Suspended single carbon nanotube resonator

How to Play a Nanoguitar



- Oscillating AC voltage $\Rightarrow$ sinusoidal electric field $\Rightarrow$ Driven "harmonic" oscillator
- Lock-in detection using δf mixing current
- Mechanical resonance peaks of the nanotube appear as peaks in the locked in signal

Detecting coverage of adsorbates

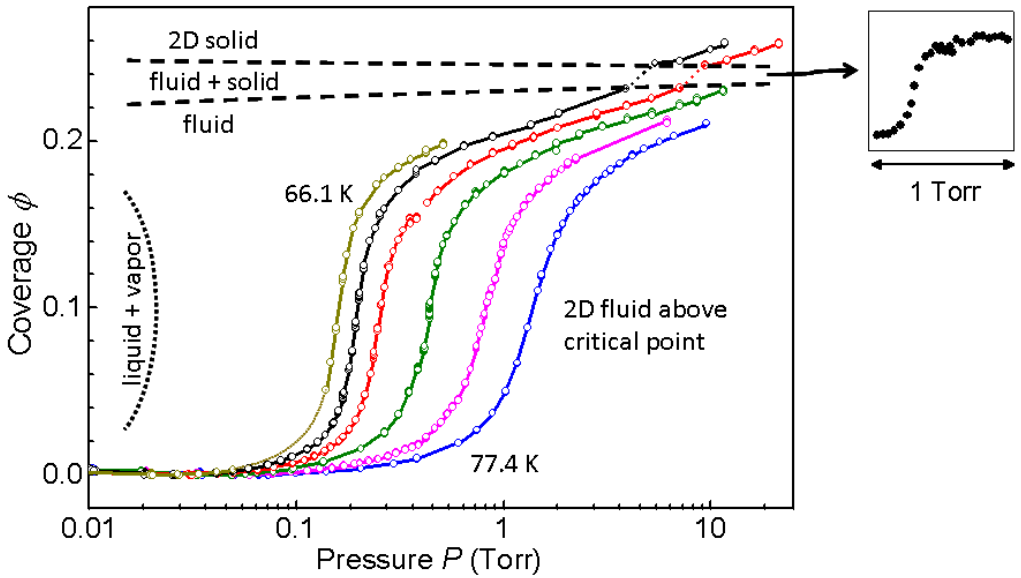
- Assumptions:
  - $f \propto \rho^{-1/2}$
  - Shifts in resonance frequency are due to changing inertial properties of resonator, not elastic properties.
- Define $\rho = m_{carbon} N_{carbon}$, $\Delta\rho = m_{adsorbate} N_{adsorbate}$, and $f_0 = \lim_{\Delta\rho \to 0} f_{res}$

$$\frac{f_{res}}{f_0} = \sqrt{1 + \frac{\Delta\rho}{\rho}}$$

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

Classical 2D Phase Behavior

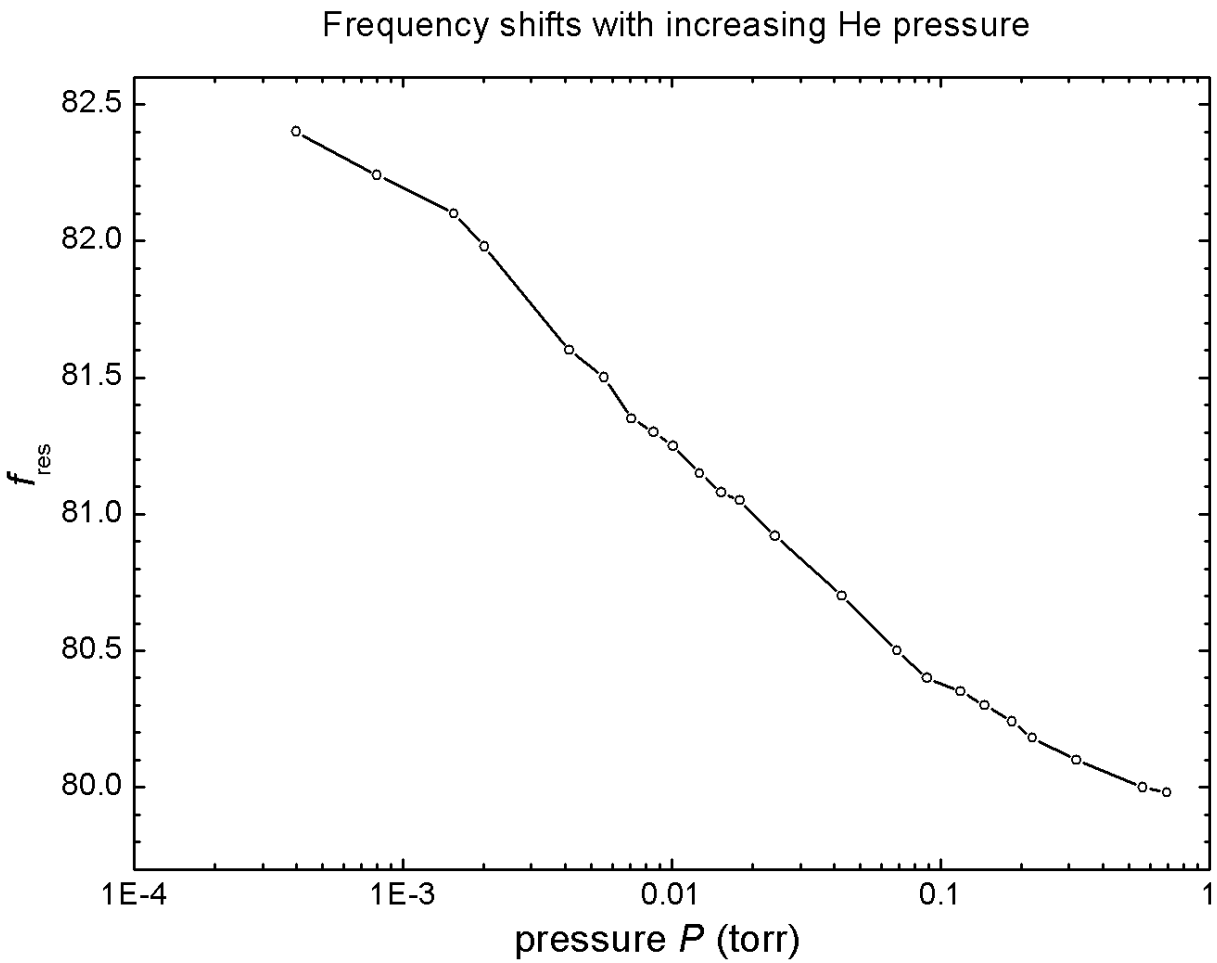
- Behave as a van der Waals substance, i.e. same phase diagram in 2D
- Inert + high polarizability = ideal candidate (noble gases)



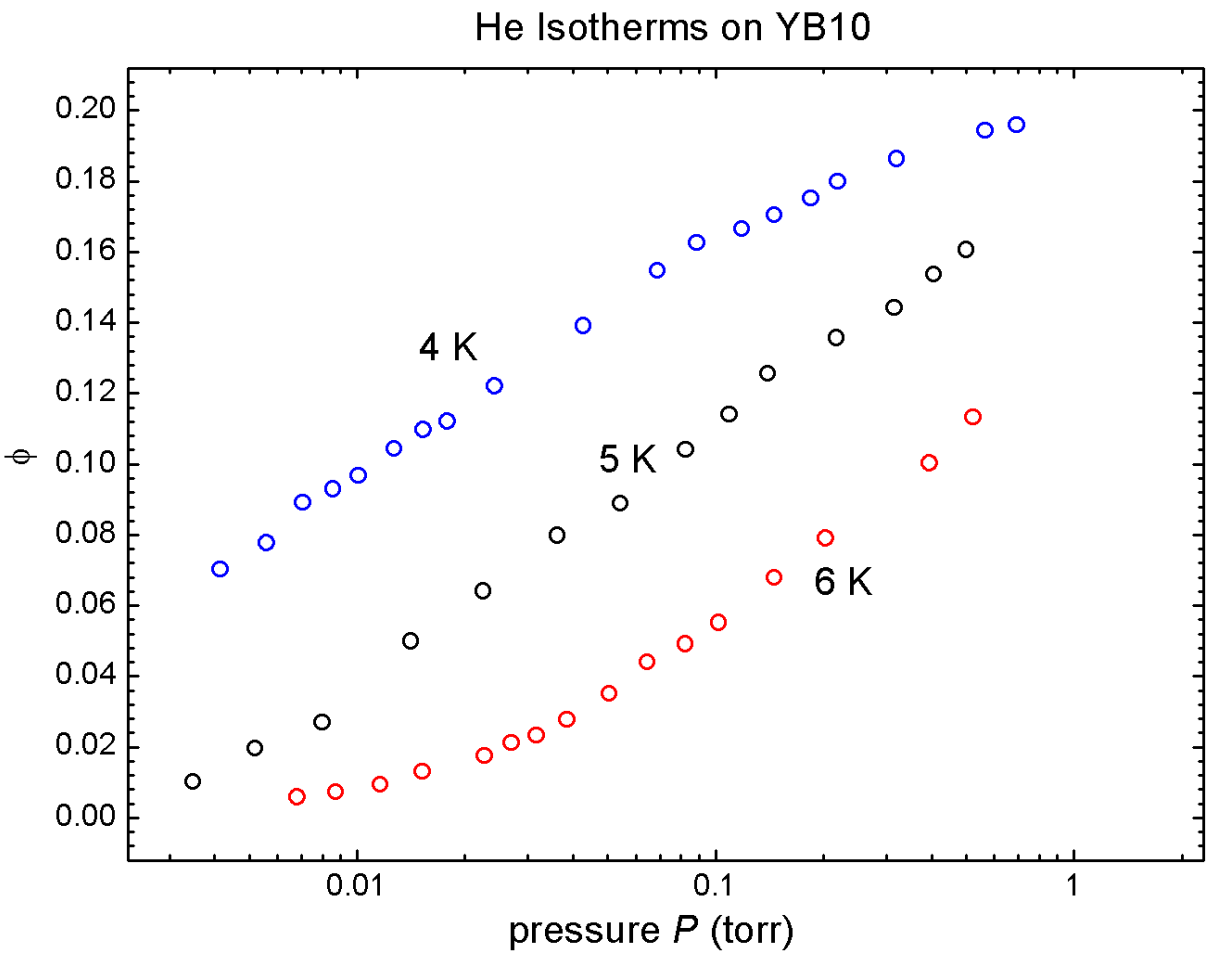
Classical vs. "Quantum" adsorbates (specifically ^{4}He)

- Classical adsorbates approximated well with the Lennard-Jones potential $\Rightarrow$ easily calculable binding energies
- Van der Waals interaction for He $<<$ classical 2D gases:
  - $\alpha_{He} = 0.204$ Å^3 vs. $\alpha_{Xe} = 4.01$ Å^3, $U_{dipole} \propto \alpha E^2$
- For He, wave function overlap may not be so well approximated by the r^{-12} in L-J
- Data from adsorption on bundles suggests ^{4}He may not adsorb well to a single nanotube; most adsorption found in interstitial channels (Wilson, Vilches, Physica B **329**, 278 (2003))

4K Isotherm



He Isotherms



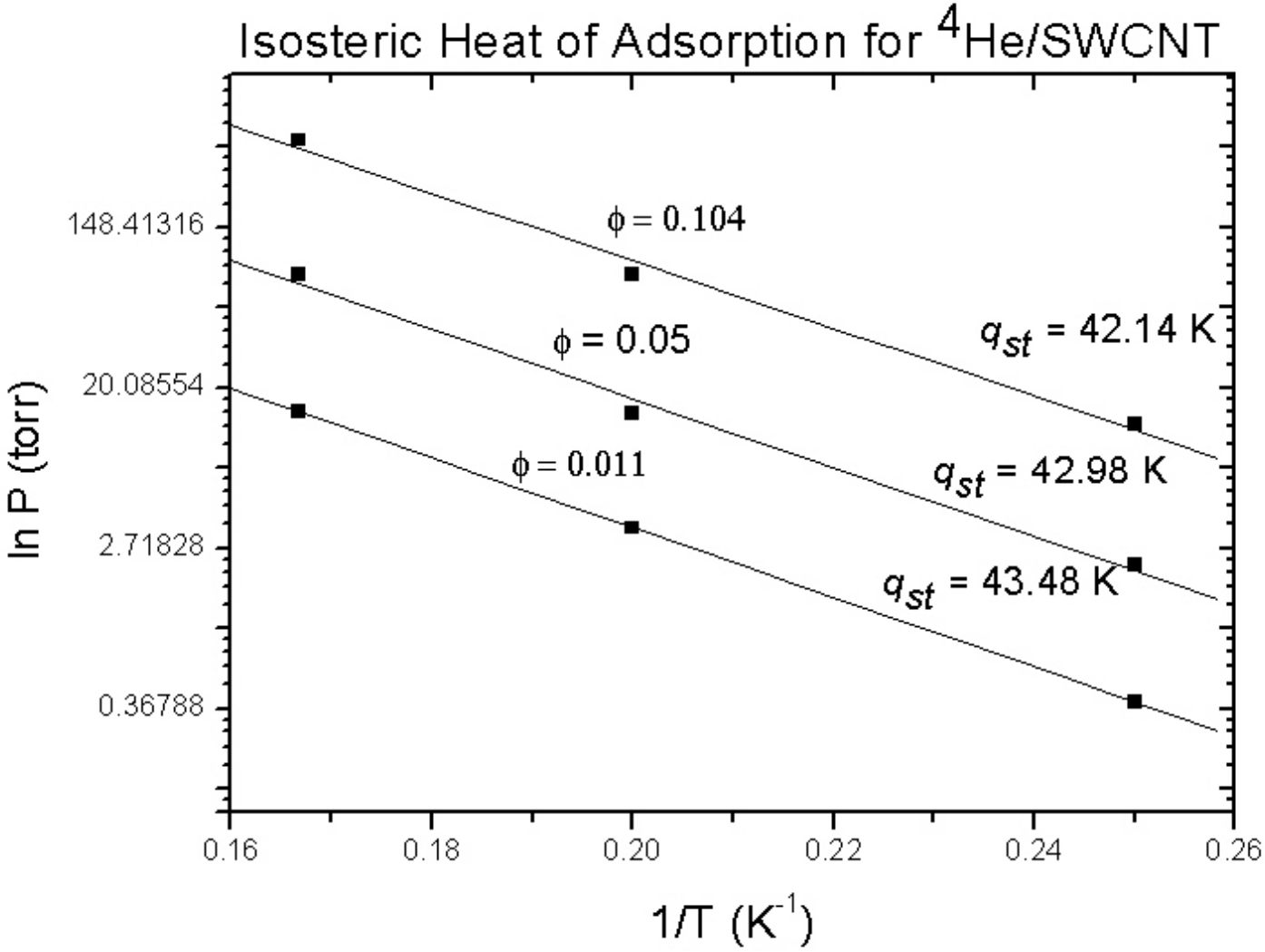
Isosteric Heat

- For a system in an equilibrium state of phase coexistence, integrated Clausius-Clapeyron equation gives (to first approximation) $P = P_0 e^{-L/kT}$
- Consider 3D gas and 2D adsorbed phase as a two phase coexistence
- Isosteric heat of adsorption:

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

- In the $\ln P$ - $1/T$ plane, curves of constant ϕ are linear (experiment)
- $\lim_{\phi \to 0} q_{st} = E_b + T\Delta S (\approx kT) - E_{zp}$

Measured Isosteric Heat



Measured q_{st} vs. "Predicted"

- $q_{st}^{exp} = 42.9$ K
- Using numerically integrated Lennard-Jones potential over cylinder (nanotube), $E_b = 142$ K for ^{4}He on a 1 nm nanotube
- Zero point energy of He/graphite ≈ 44 K
- $\Rightarrow q_{st}^{th} \approx (142 + 5 - 44)$ K ≈ 103 K
- Evidently true quantum calculation needed to resolve discrepancy:
  - Wave function overlap may push r_0 further from tube $\Rightarrow$ E_b and E_{zp} decrease

Summary and Acknowledgments

- Preliminary adsorption data collected with ^{4}He on a single nanotube
- Isosteric heat (on nanotube) inconsistent with models which work for less quantum gases
- To try: Adsorb ^{4}He on different nanotube, find q_{st} dependence on diameter

Thank You

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