Enabling Discovery of Materials With a Suitable Heat of H_2 Adsorption

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Overview

Timeline

- Project start date FY05
- Project end date FY10
- ~20% complete

Budget

- Total project $3,948,220
  - DOE share $3,158,575 (80%)
- FY05 funding $300,000
- FY06 funding $475,000

Barriers

- Technical Barriers- Hydrogen Storage
  - B. Weight and Volume
  - C. Efficiency
  - E. Refueling time
  - M. Hydrogen Capacity and Reversibility
  - O. Test Protocols
  - Q. Thermal Management

Partners

- Current interactions: NREL, ORNL, Penn State
- Anticipated collaborations: Rice University, Duke University, University of North Carolina

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Approach: How can we enable discovery of materials with a suitable heat of H_2 adsorption?

- Rapid, inexpensive measurement techniques – accelerated materials/process development towards meeting DOE system targets for hydrogen storage
  - Sorption capsule technique
- Accurate measurement techniques – provide critical guidance to center partners that enables new materials development
  - Differential pressure adsorption
  - Correction for helium adsorption effects on H_2 isotherms
- General quantitative computational models for new materials– efficient materials discovery/optimization towards meeting DOE system targets for hydrogen storage
  - Realize more practical overlap between computational and experimental work (eg. modeling excess adsorption)
  - Predictive modeling of new types of materials
  - Optimization of existing materials

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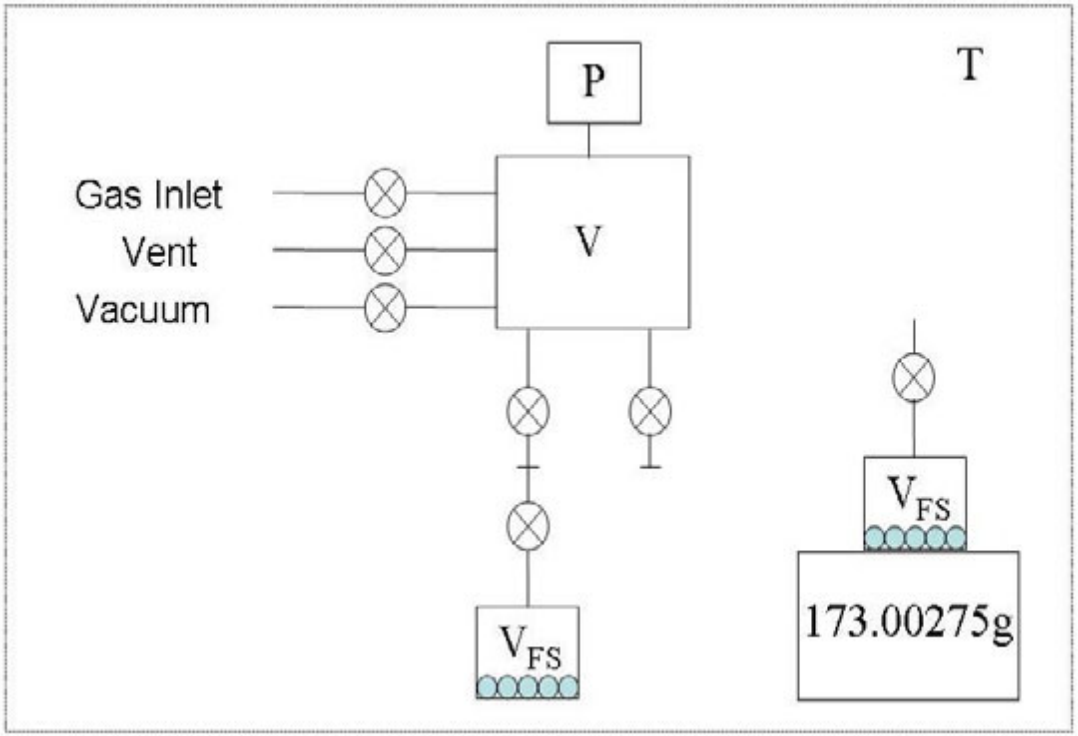
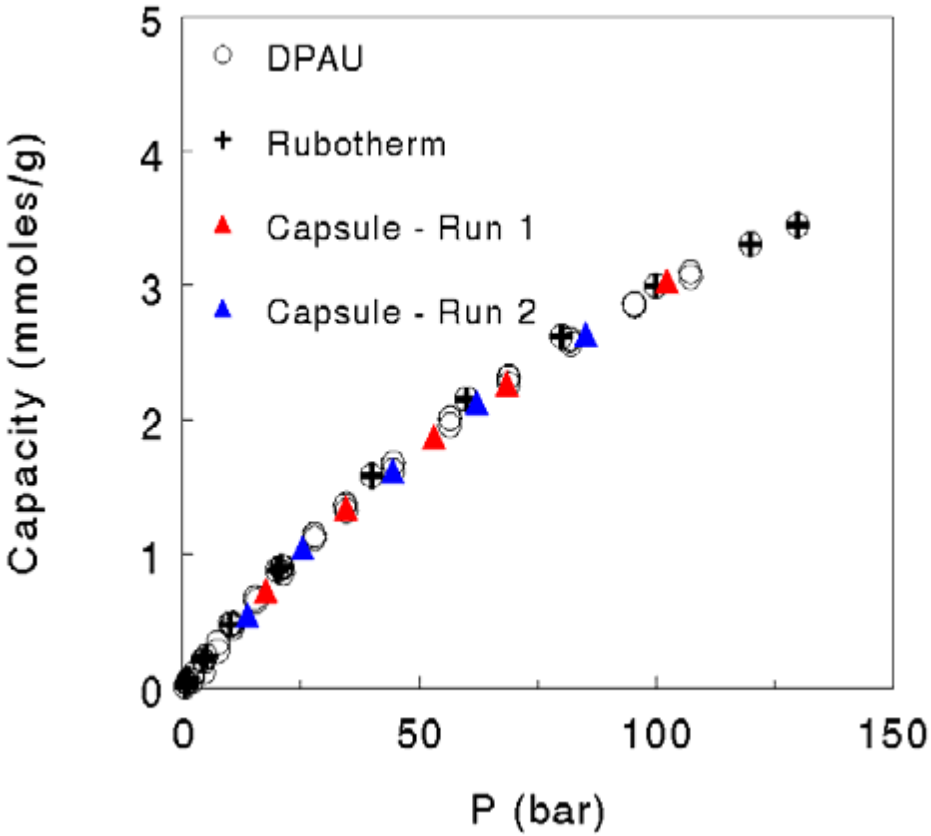
Technical accomplishments: sorption capsule technique

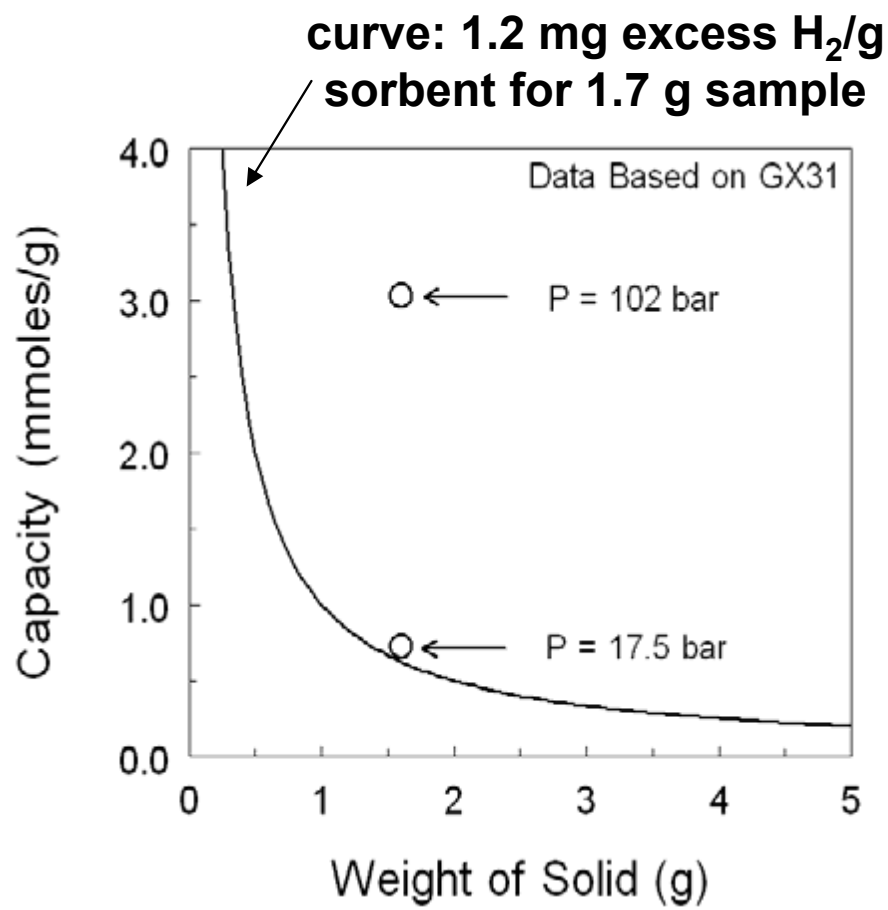


- Potentially useful for rapid screening of total hydrogen storage (excess hydrogen + gaseous hydrogen)
- Also can be used to measure isotherms if "free space" is determined by He expansions
- Very inexpensive equipment needed for implementation

A hydrogen storage measurement technique that could accelerate new materials development

Technical accomplishments: H_2 isotherms on GX-31 activated carbon at 25°C by three independent methods including the capsule technique





Capsule technique validated and representative limit of operation established

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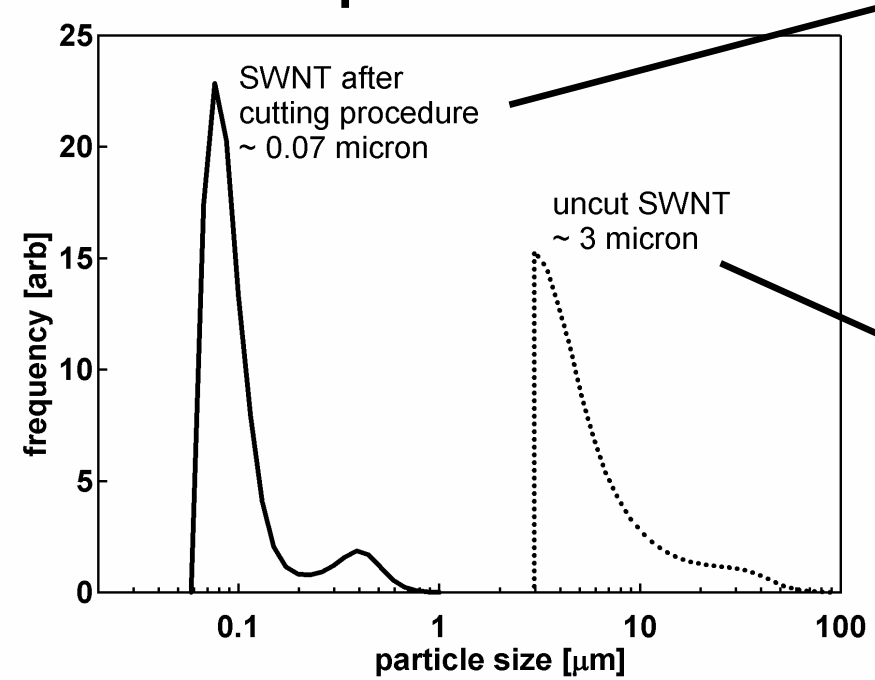
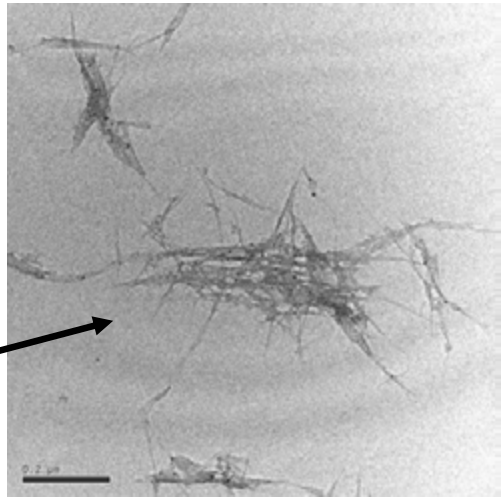
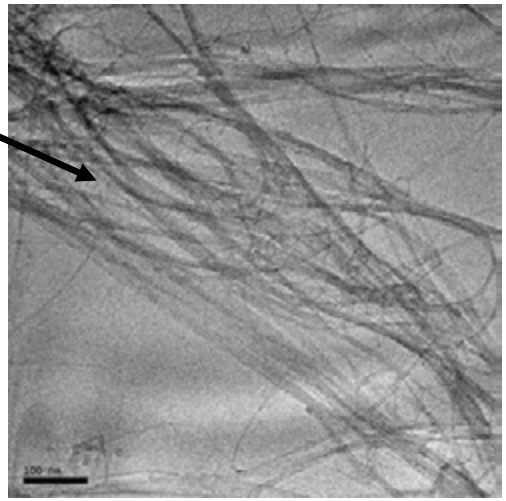
Activation and adsorption characterization of carbon-based materials: "Tailoring" singlewalled carbon nanotubes for hydrogen storage

Laser light scattering profile of SWNT samples before (dotted line) and after (solid line) a non-destructive cutting procedure







Transmission Electron Microscopy

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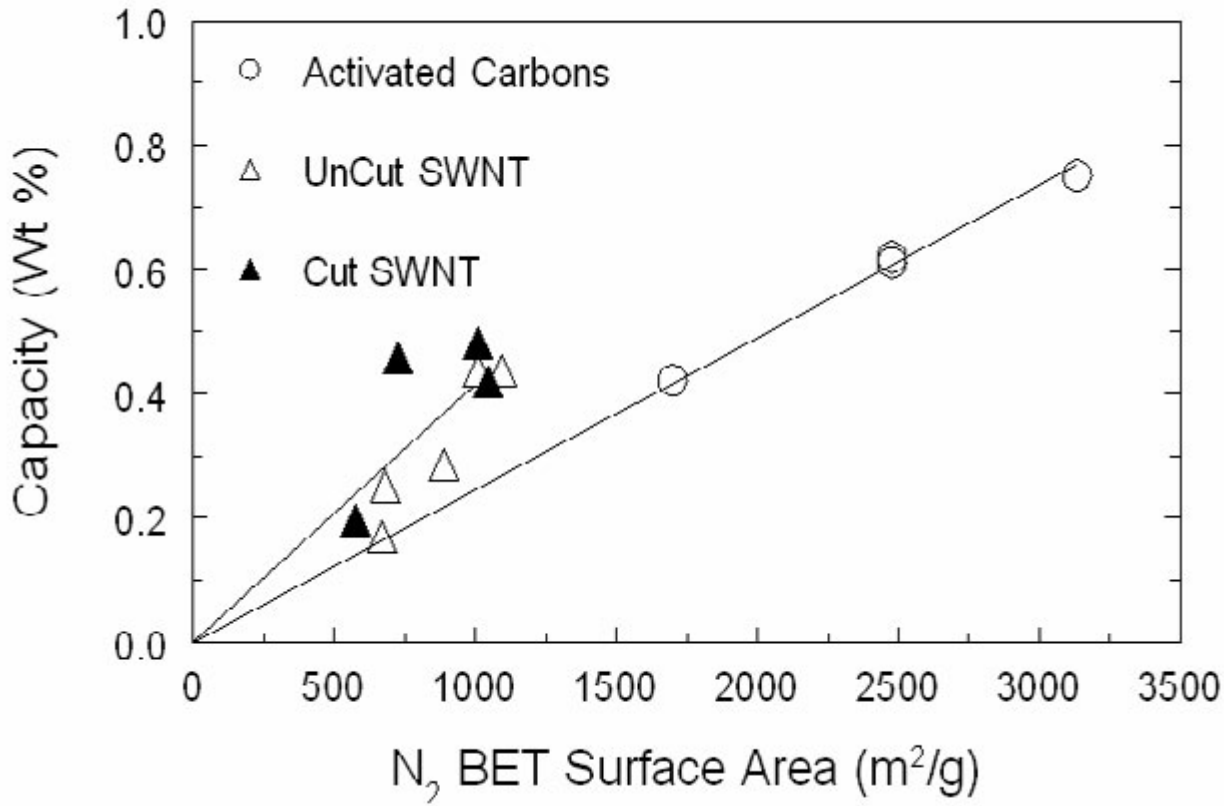
Technical accomplishments: Hydrogen capacity at 25°C and 107 bar as a function of N_2 BET surface area



Heat of adsorption of carbon nanotubes is higher than activated carbon – more substantial hydrogen adsorption at ambient temperature is important for meeting DOE system targets

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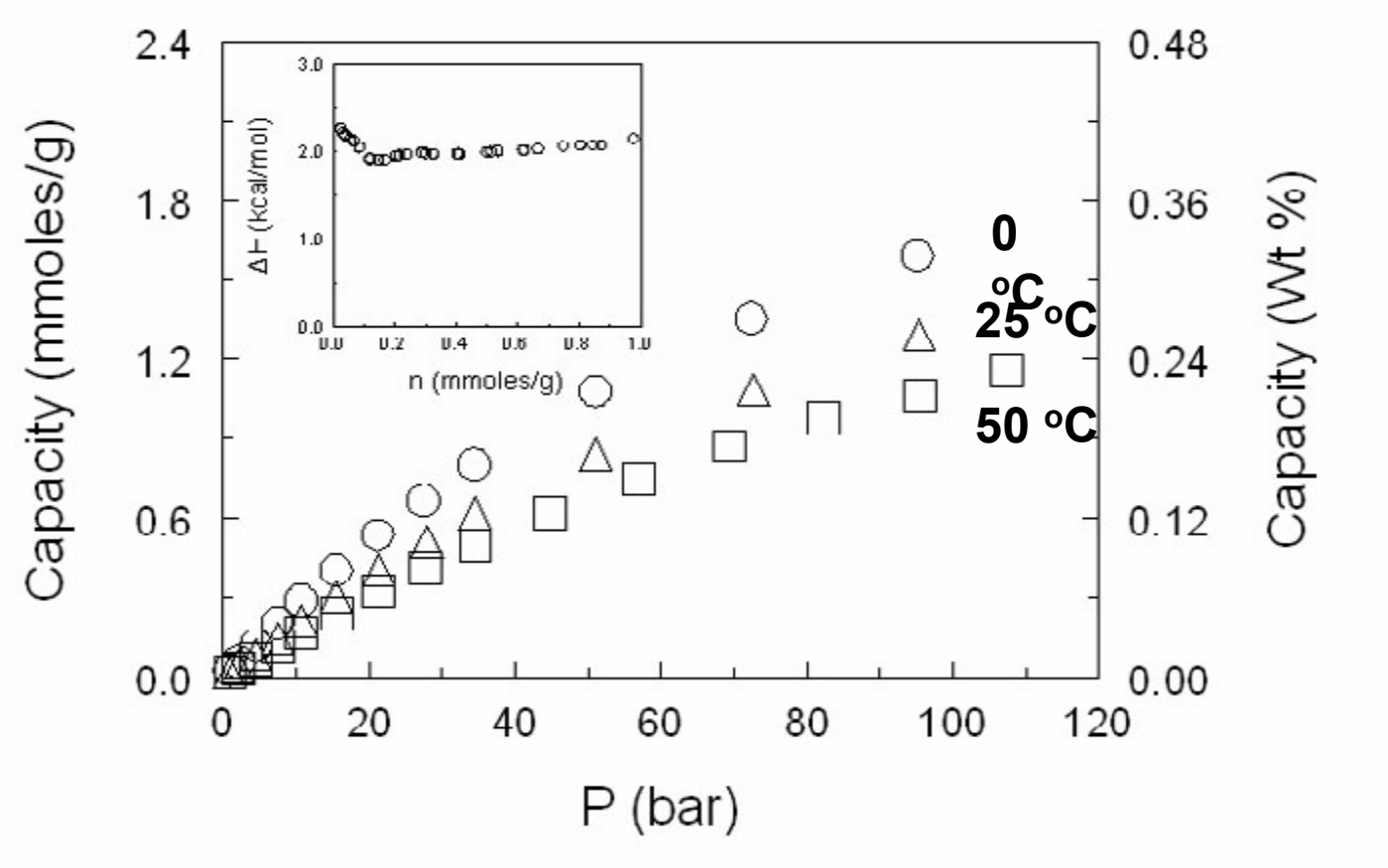
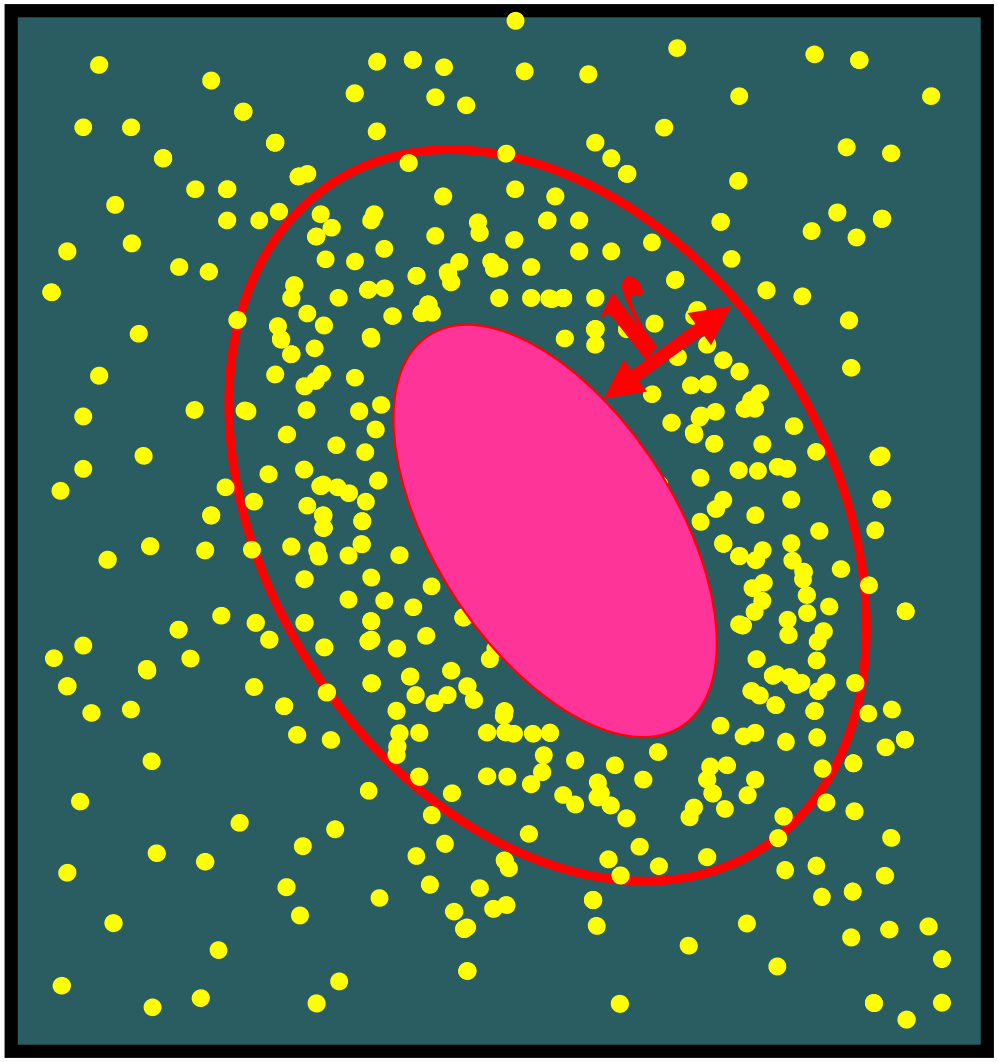
Technical accomplishments: Hydrogen isotherms on singlewalled carbon nanotubes and isosteric heat of adsorption



Heat of adsorption is higher than activated carbon – but still not high enough for substantial capacity at near-ambient temperature from physical adsorption alone

Technical accomplishments: A new approach for modeling Gibbs excess adsorption



- Adsorption strength and capacity are distance-dependent
- Distance-dependent adsorption energy and effective capacity can be expressed in terms of minimum distance distribution function

Application of approach to H_2 Adsorption in SWNT bundles: Objectives and method

- Understand the difference between homogeneous and inhomogeneous SWNT bundles for H_2 adsorption
- Understand the effects of nanotube bundle thickness

- Molecular dynamics simulation with a curvature-dependent force field (Physical Review Letters, 89 146105, 2002)
- Simulation time: 50 picoseconds
- Room temperature (300 K)

Finite SWNT bundles represent an excellent hydrogen storage material model for testing our new computational methods – our ultimate goal is to enable predictive computational modeling of new materials that can meet DOE system targets

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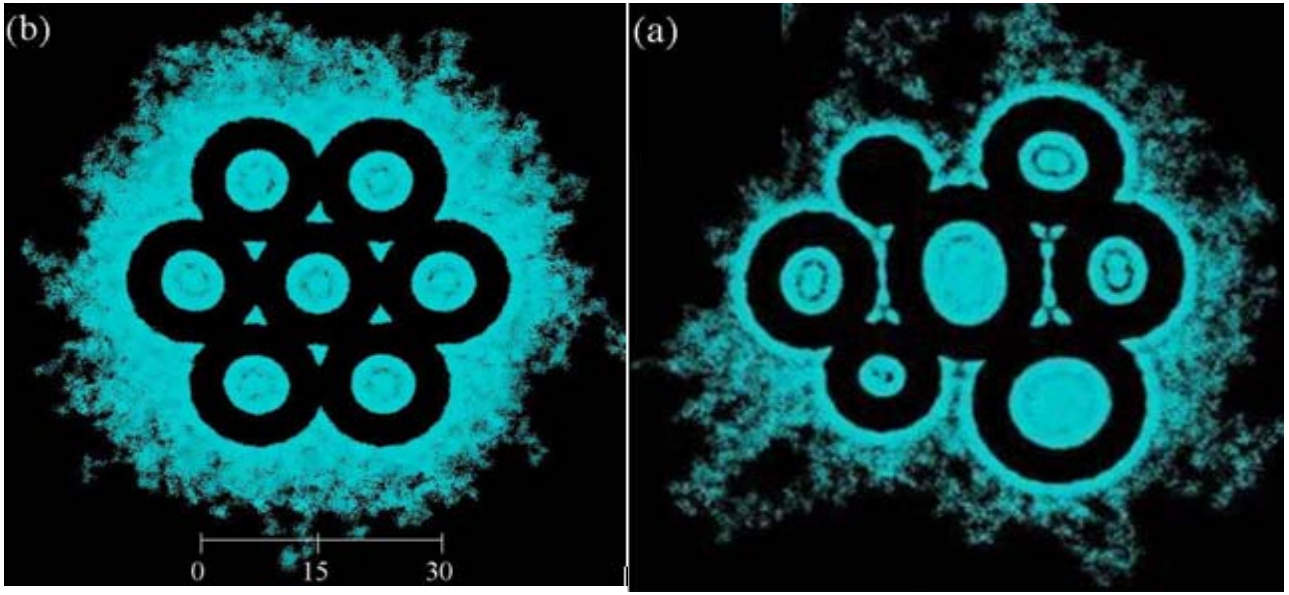
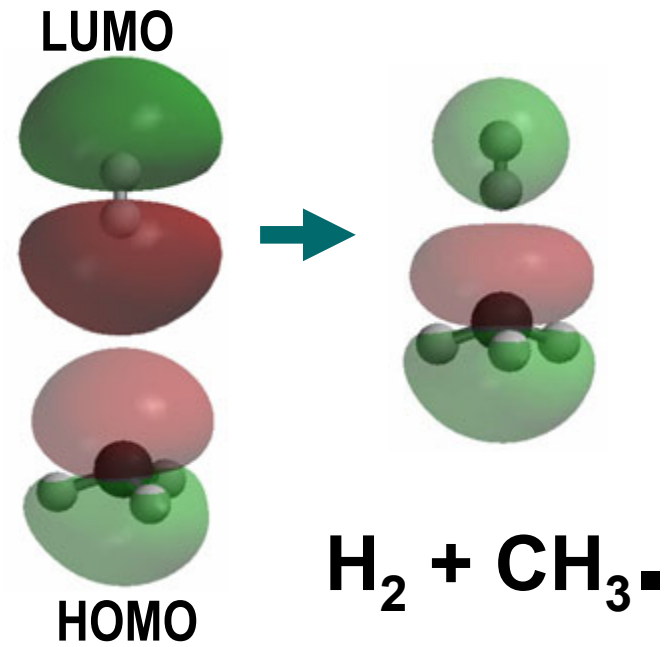
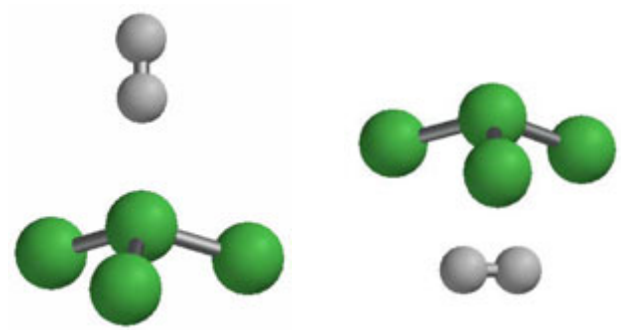
Technical accomplishments: adsorption density maps





Seven (9,9) homogeneous SWNT in bundle

Seven inhomogeneous SWNT in bundle



Nanotube diameter: 12.2Å

Average nanotube diameter: 12.2Å

More H_2 molecules are adsorbed within close proximity of inhomogeneous nanotube bundles

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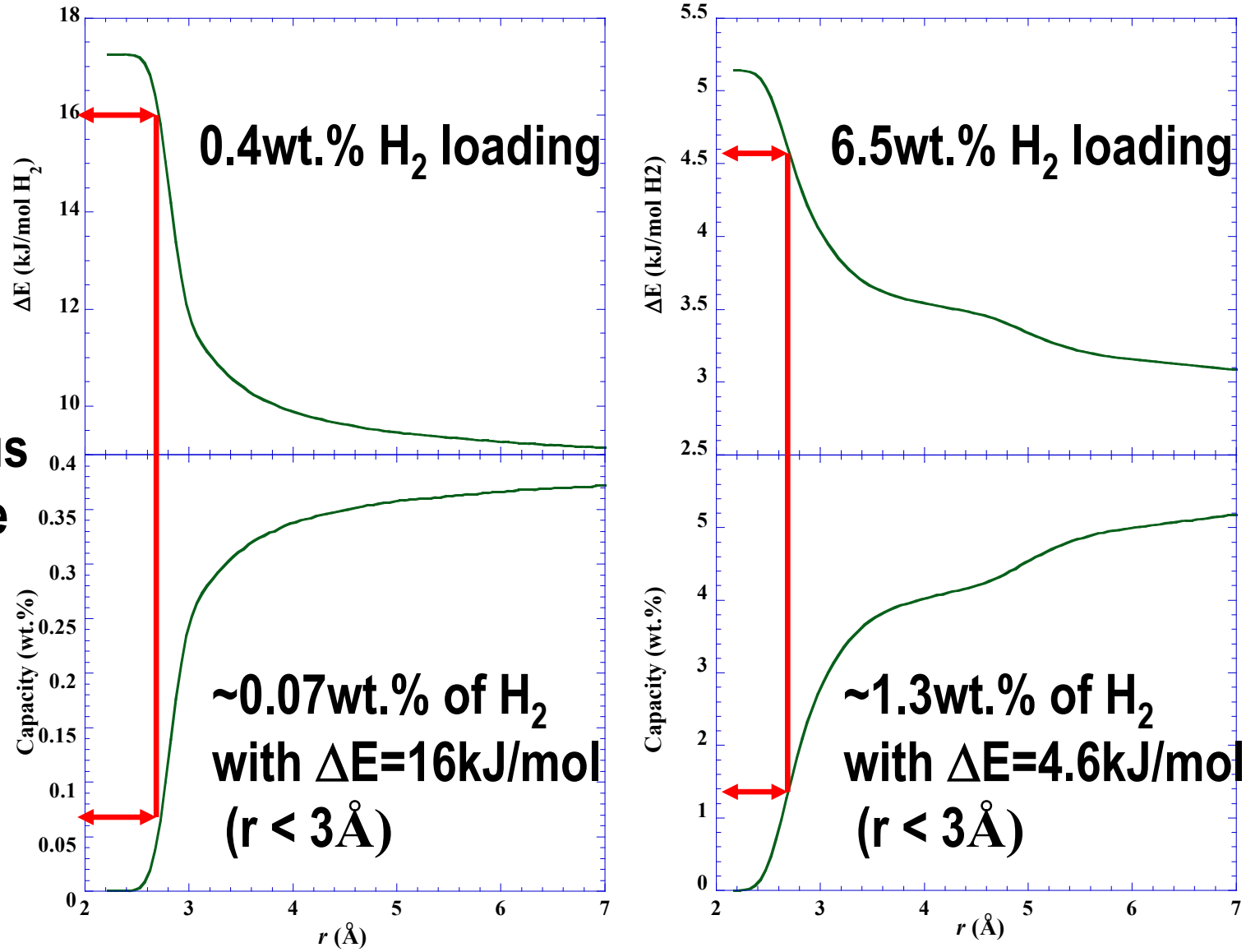
r-Dependent Adsorption Energy vs. Capacity

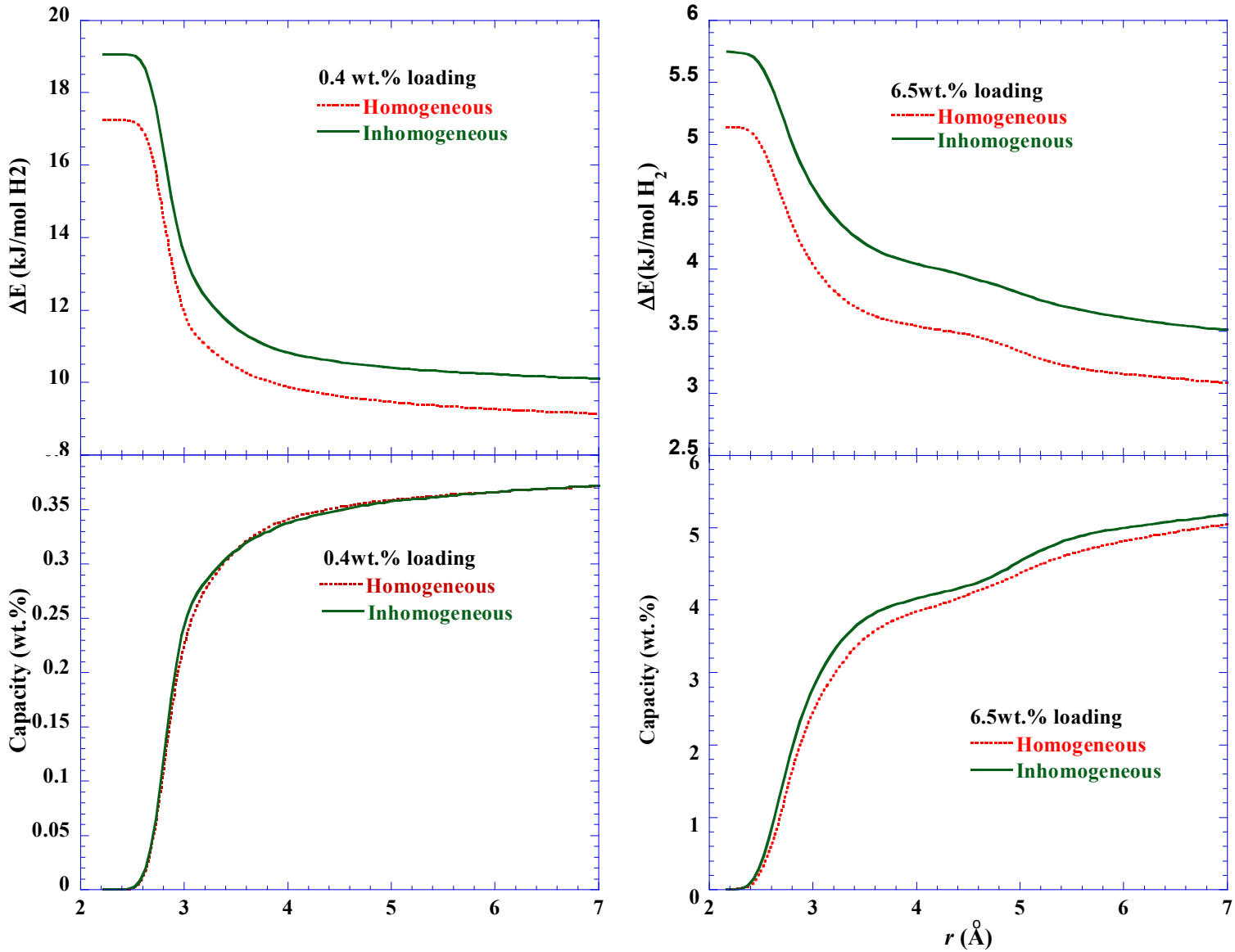
Homogeneous 7 tube bundle



- Adsorption energy decreases with H_2 loading
- Only a small percentage of H_2 is adsorbed strongly

Comparison of Homogeneous and Inhomogeneous SWNT Bundles

7-nanotube bundles



Stronger adsorption in inhomogeneous SWNT bundle

Predictive computational modeling of new materials with potential for higher heats of adsorption: boron and nitrogen substituted graphite

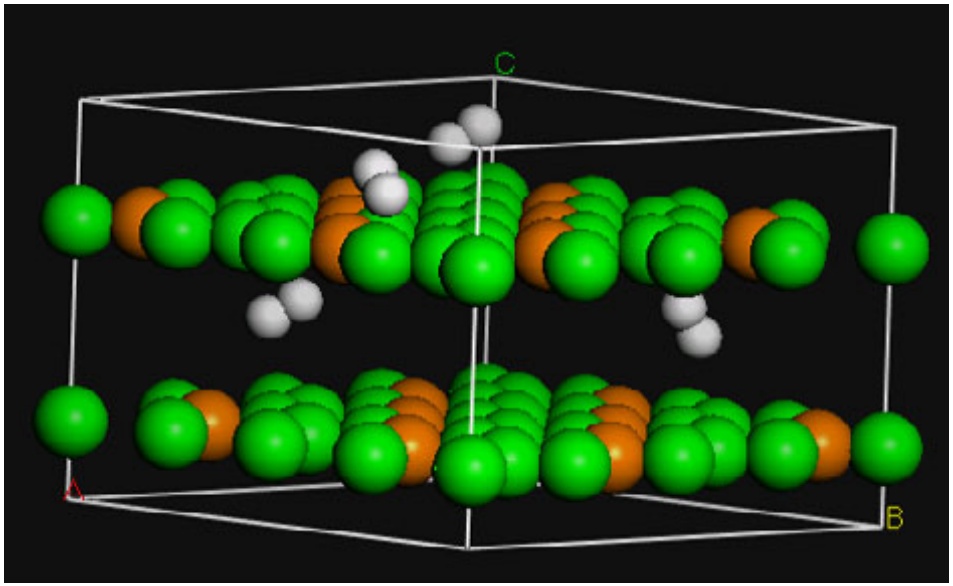
Unit Cell: $C_xY_{64-x} \bullet 4H_2$ (Y=B,C,N)

Optimized inter-sheet Distance:

$C_{64} \bullet 4\,H_2$: 4.87Å

$C_{48}B_{16} \bullet 4\,H_2$: 5.10Å

$C_{48}N_{16} \bullet 4\,H_2$: 4.64Å



- **Ab initio molecular dynamics simulation at room temperature for 5 picoseconds, interaction forces calculated with local density functional theory**

Our computational methods and materials are complementary to other CoE partner efforts (PSU, NREL, Rice)

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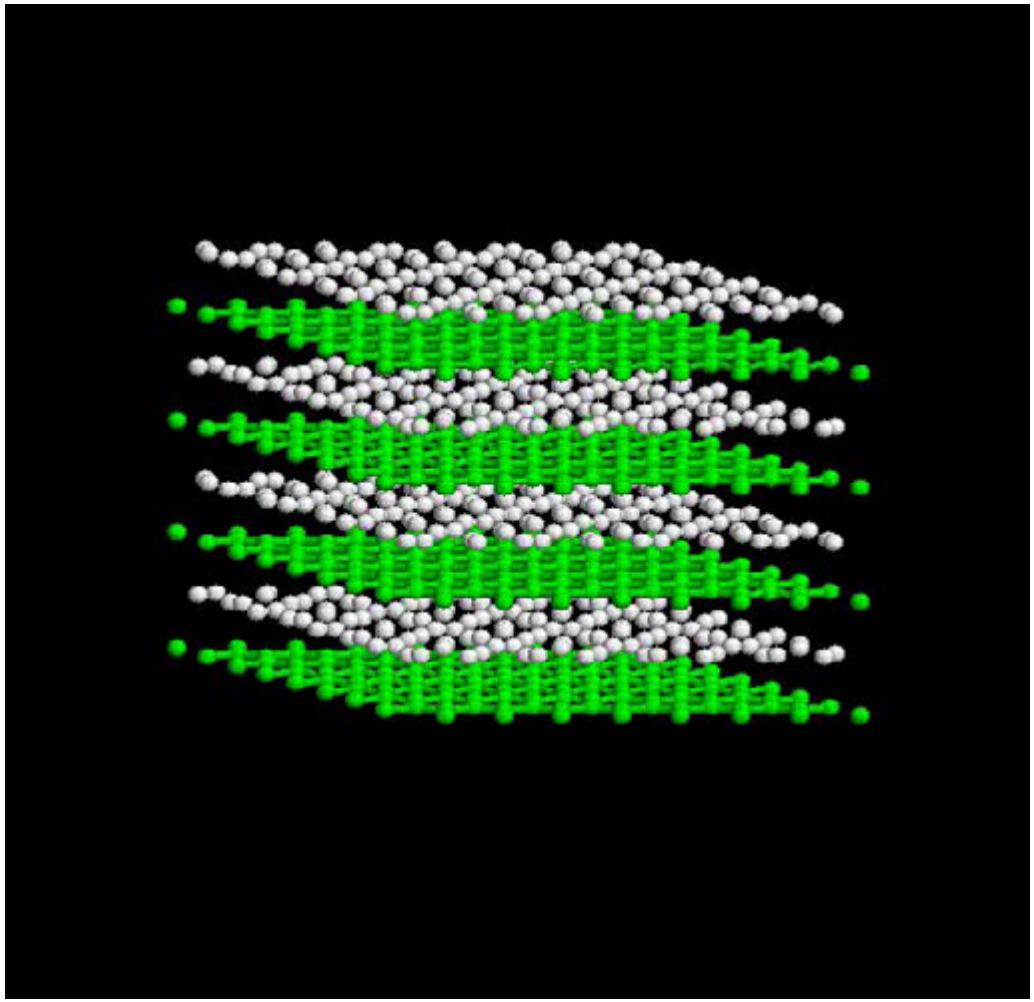
Molecular dynamics: H_2 in graphite at 77K



- Unit Cell: C_{64}•$32H_2$
- Inter-sheet distance: 4.914Å
- The calculated H_2 adsorption energy: -4.39kJ/mol H_2, is in good agreement with experimental values for heat of adsorption of hydrogen on graphite (ca. 4 kJ/mol H_2)

A successful test of our computational methods on a known system before beginning predictive modeling of new boron or nitrogen-containing materials

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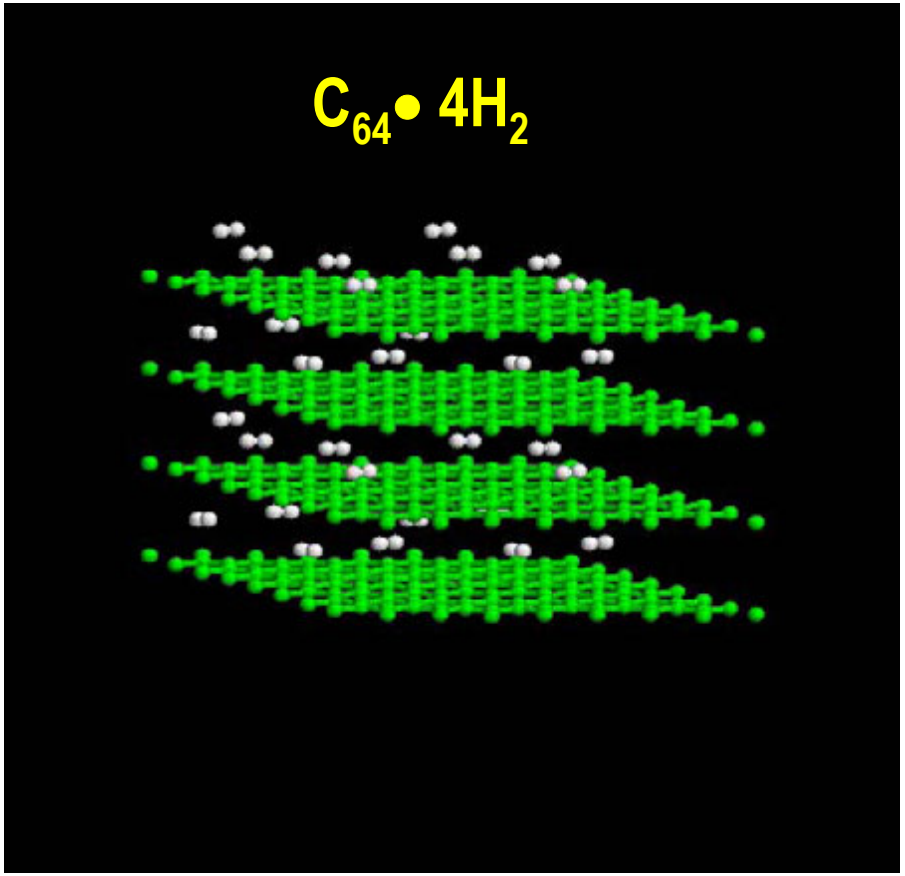
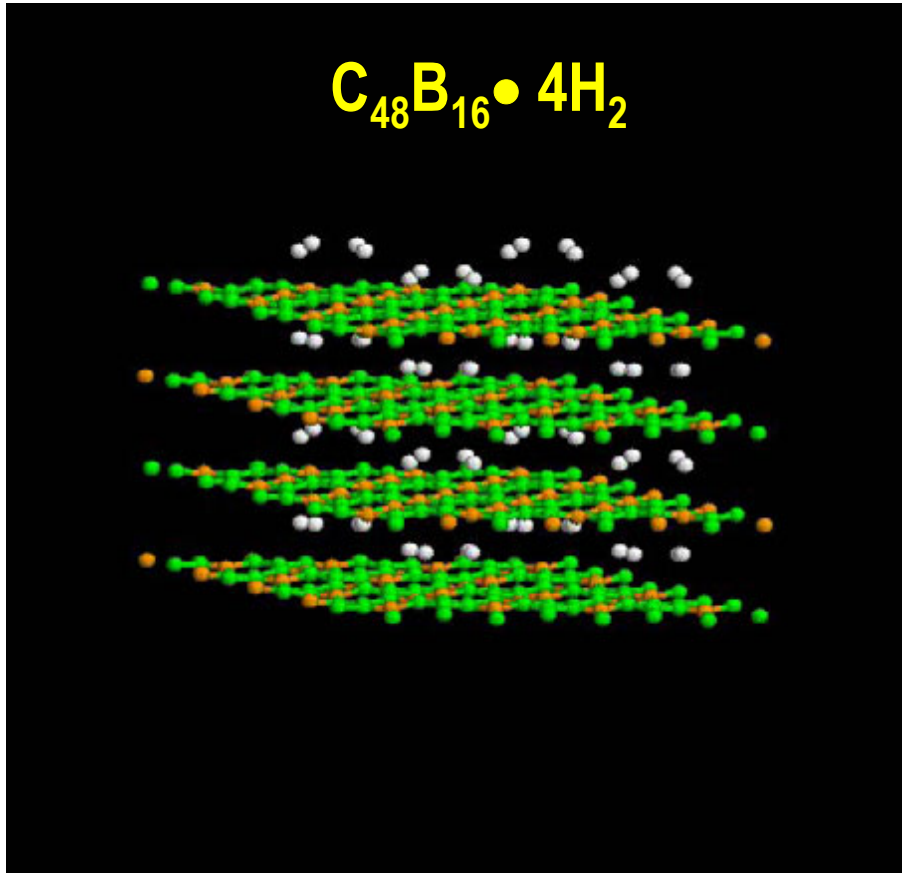
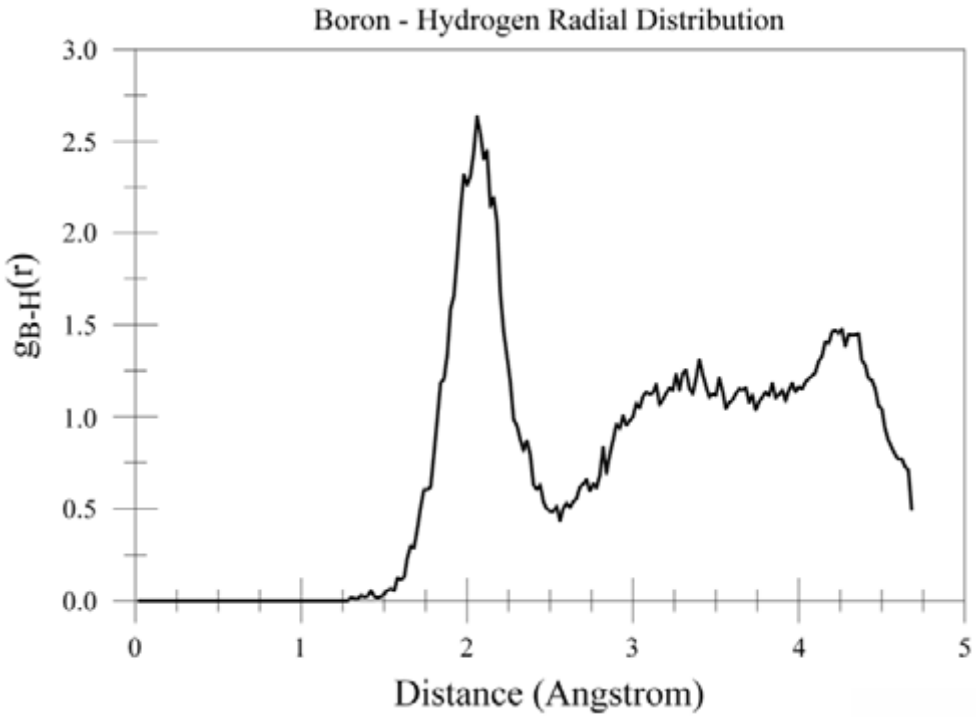
Technical accomplishments: Ab initio molecular dynamics simulations

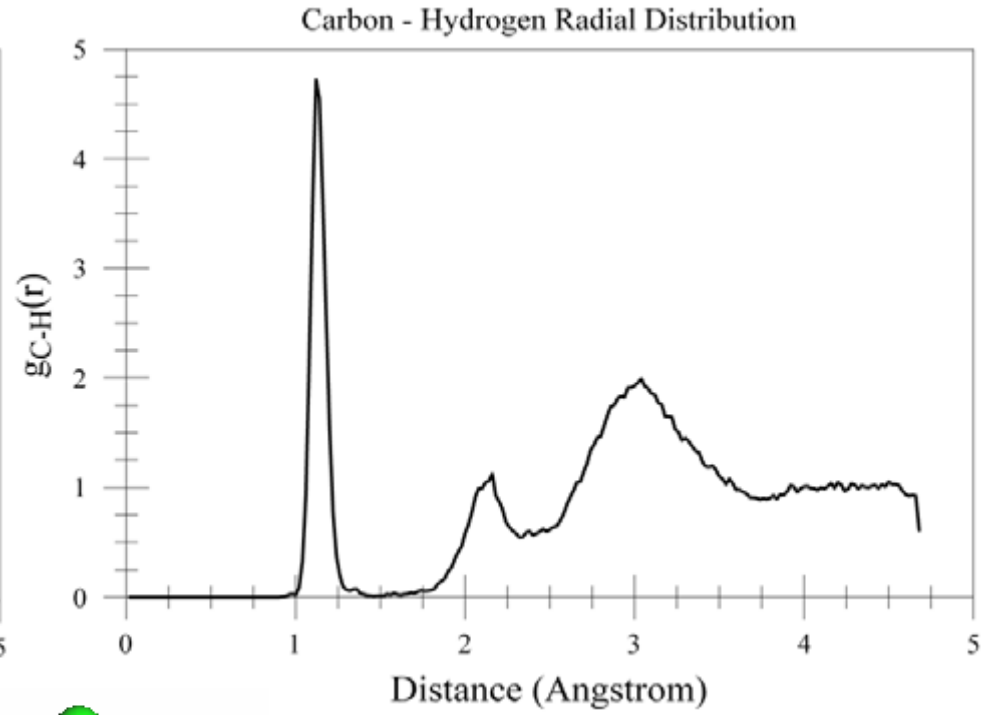




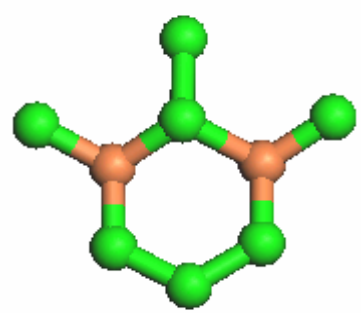
	C_{64} • 4 H_2	$C_{48}B_{16}$• 4 H_2	$C_{48}N_{16}$ • 4 H_2
ΔH (kJ/mol H_2)	no binding	-17.8	no binding

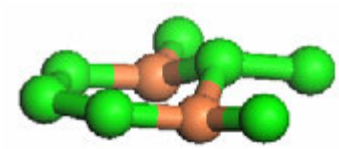
Technical accomplishments: Radial distribution functions from *ab initio* molecular dynamics simulations of hydrogen adsorption on boron containing carbon ($C_{48}B_{16}$)





∠BCB ~ 105° – 115°





These boron-containing carbons have a substantially stronger interaction with hydrogen than the pure carbon analog

Summary

- We have developed new computational methods for hydrogen storage material discovery
  - The methods enable predictive modeling of hydrogen adsorption in carbon-based materials
  - The methods provide a more accurate model of the H_2 adsorption energies than previous methods
- We have established the accuracy of our high pressure isotherm measurements
  - Our expertise and equipment time has been made available to all interested CbHS center partners
- We have invented a new hydrogen storage materials measurement method
  - This method is designed to allow rapid screening of new materials (physisorption and/or chemisorption)
  - The details on design and operation have been transferred to interested CoE partners for potential implementation in their labs to accelerate new hydrogen storage materials discovery

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Future Work

- Application of computational methods to new materials of interest to CbHS partners
  - Ab initio molecular dynamics study on hydrogen spillover mechanism (potential >7 wt. % hydrogen storage)
- Increased collaboration with partners on accurate hydrogen adsorption measurements
  - Investigate extending our capability from near-ambient temperatures to cryogenic temperatures (eg. >7 wt. % hydrogen storage in literature using MOF)
  - Complete development of high temperature pycnometer for correction of helium adsorption effects on hydrogen isotherms (preliminary – up to 25% change in measured capacity)
- Initiate experimental program in FY06 on new hydrogen storage materials
  - Resource dependent
  - Collaborations expected (eg. on B, N-containing carbon materials)

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Back-up Slides (not presented or for reference)

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Acknowledgements

- Hydrogen adsorption measurements/materials:
  - Michael Kimak
  - Peter McKeon (undergraduate summer intern)
  - Gennady Dantsin
  - Mary Haas
- Computational modeling and methods development:
  - Prof. Steven Stuart (Clemson Univ.)
  - M. Todd Knippenberg (graduate intern)

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Publications and Presentations

- **Publications**
  - **"Tailoring singlewalled carbon nanotubes for hydrogen storage" Journal of Materials Research, 20, 3214 (2005).**
  - **"Accurate Hydrogen Sorption Measurements via Differential Pressure Analyses" (submitted)**
  - **"A Low Cost Sorption Experiment Designed for the Support of H_2 Storage Materials Development" (submitted)**
  - **"On the Effective Capacity of Finite Bundles of Single Walled Carbon Nanotubes for Hydrogen Adsorption" (submitted)**
- **Presentations**
  - **"Hydrogen Storage with Carbon Materials – *Quo Vadis?*": International Partnership for a Hydrogen Economy Hydrogen Storage Workshop, 6/05, Invited Presentation**
  - **"Advanced Hydrogen Sorption Measurement Techniques: Application to Tailored Singlewalled Carbon Nanotubes": Materials Research Society Fall Meeting, 11/05, Invited Presentation**
  - **"Enabling Discovery of Materials With Higher Heat of Adsorption": FreedomCAR tech team review meeting 3/06**

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Critical Assumptions and Issues

- Hydrogen storage materials will be discovered that have an adequate heat of adsorption to significantly improve the volumetric efficiency of hydrogen storage systems at near-ambient temperatures
  - This will require higher heats of adsorption than known hydrogen storage materials
  - We have observed that modification of known materials (eg. boron-substituted graphite) can have profound effects on the heat of adsorption
- A working hydrogen storage system prototype can be designed and constructed that achieves necessary gravimetric and volumetric hydrogen storage densities
  - This will require discovery of a new material with high hydrogen storage capacity under practical operating conditions of pressure and temperature
  - However, also required is an efficient thermal management system to allow rapid charging and discharging
  - Some engineering principles from existing metal hydride hydrogen storage systems may be transferable

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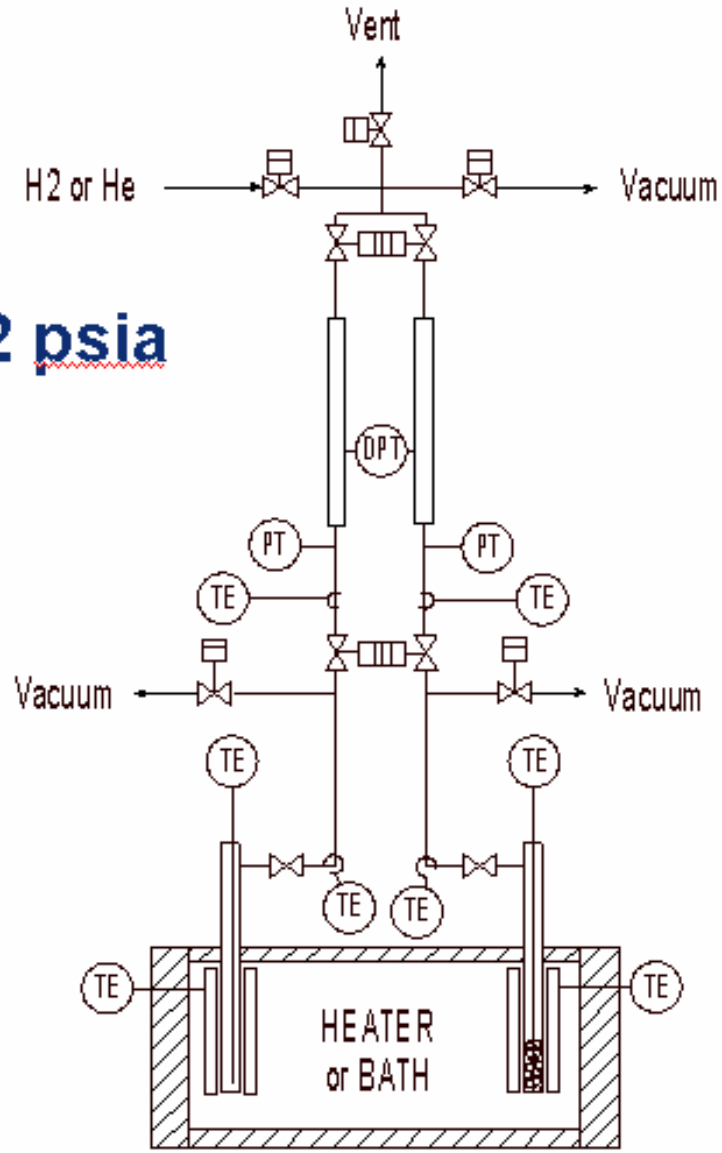
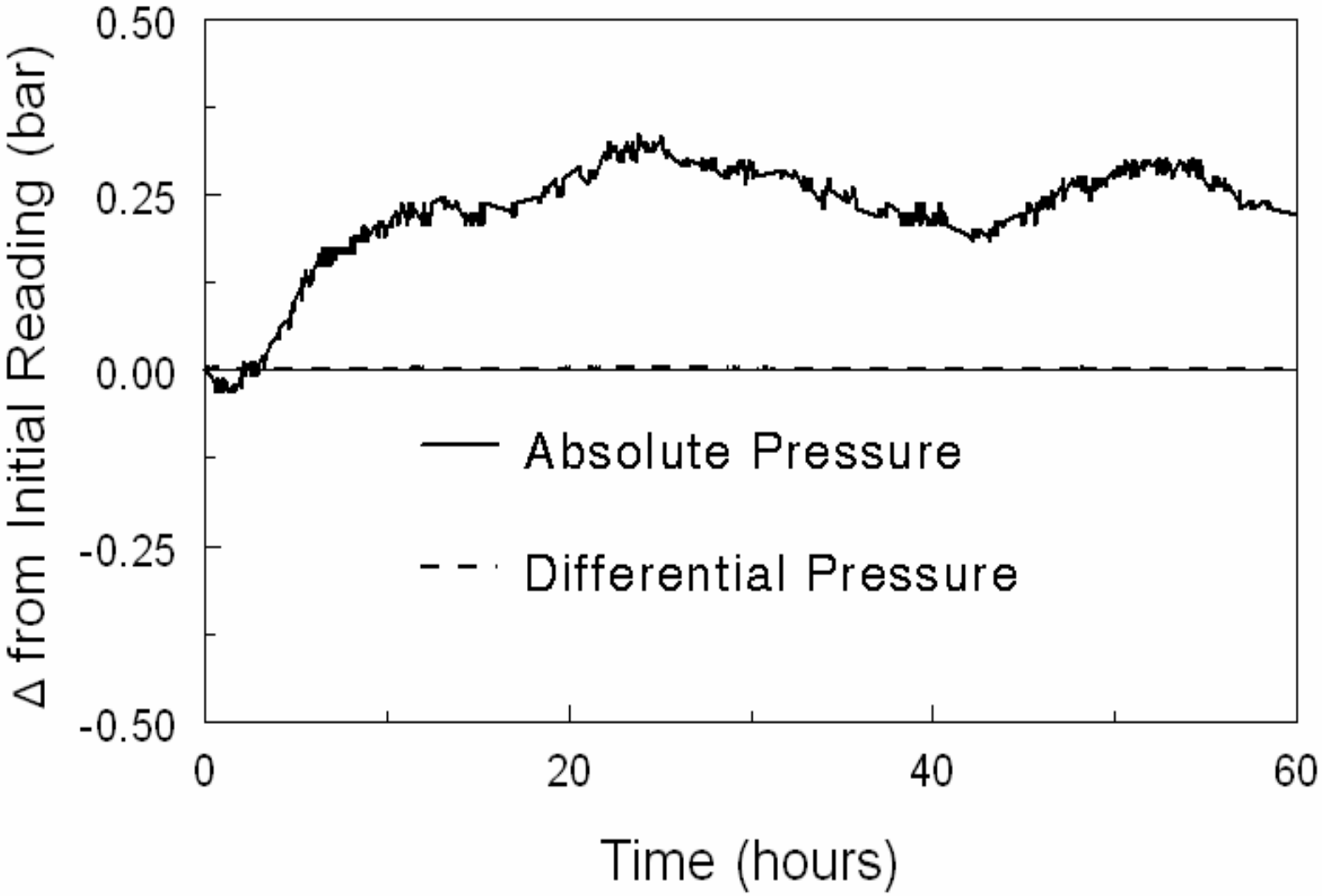
Reference: Differential Pressure Adsorption Unit (DPAU)

Accuracy of 0.02 psia independent of pressure



Differential pressure measurement unaffected by lab temperature variation



P = 68.9 bar

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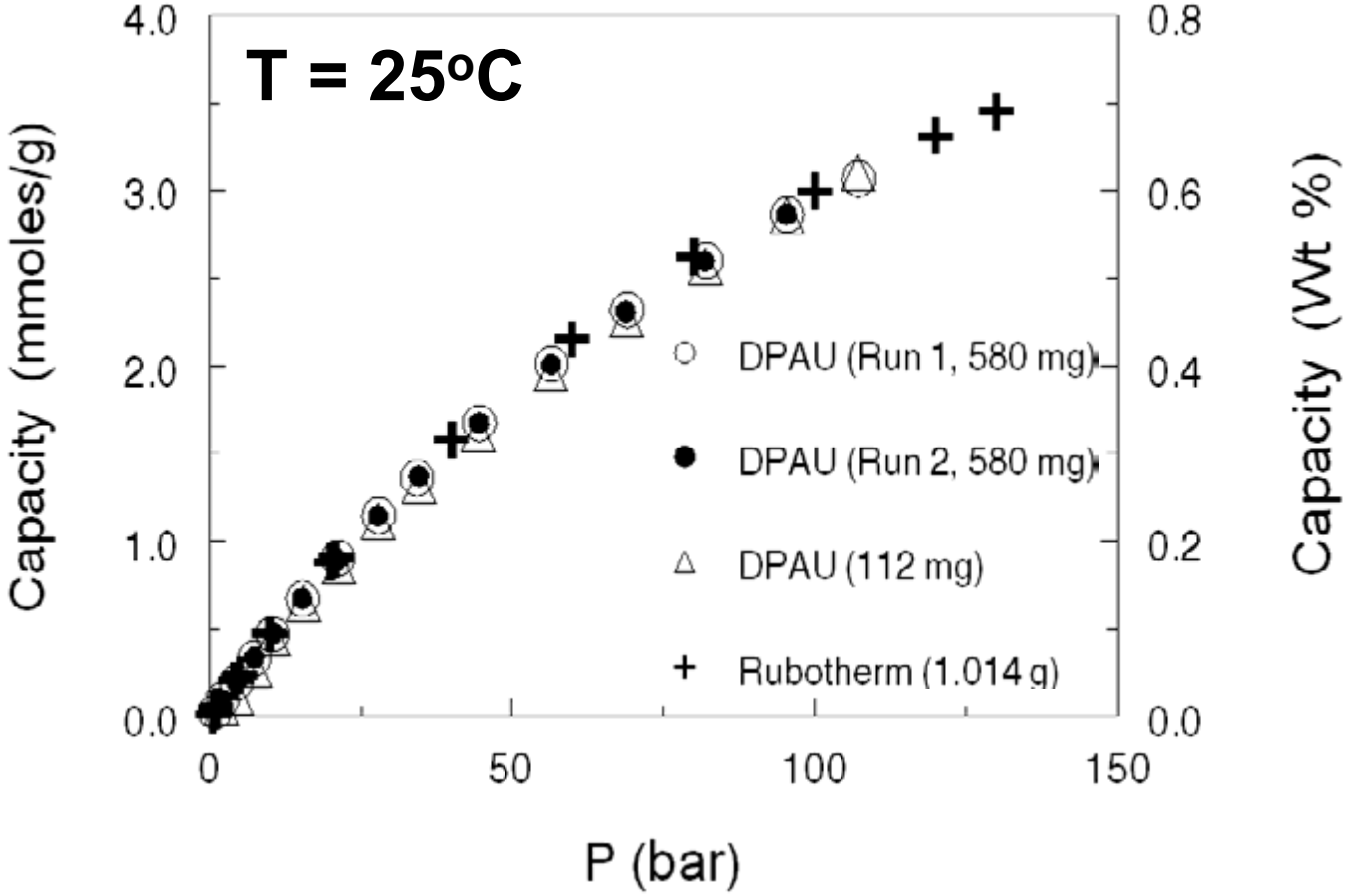
Hydrogen Isotherm on GX31 Activated Carbon: Benchmarking DPAU against Gravimetric Data



We have successfully measured near-ambient temperature isotherms on carbon samples as small as <60 mg

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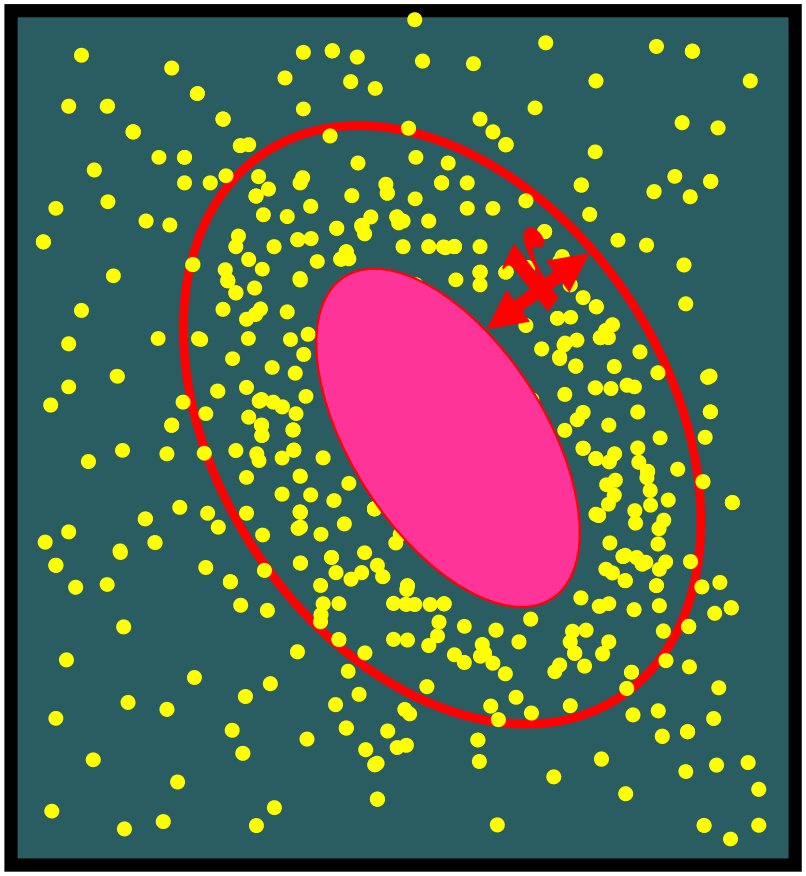
Reference: Gibbs Excess Adsorption

$$\Delta E_{ad}(r) = n(r)\varepsilon_{gas} + \varepsilon_{sub} - \left\{\varepsilon_{sys} - \left[N - n(r)\right]\varepsilon'_{gas}(r)\right\}$$



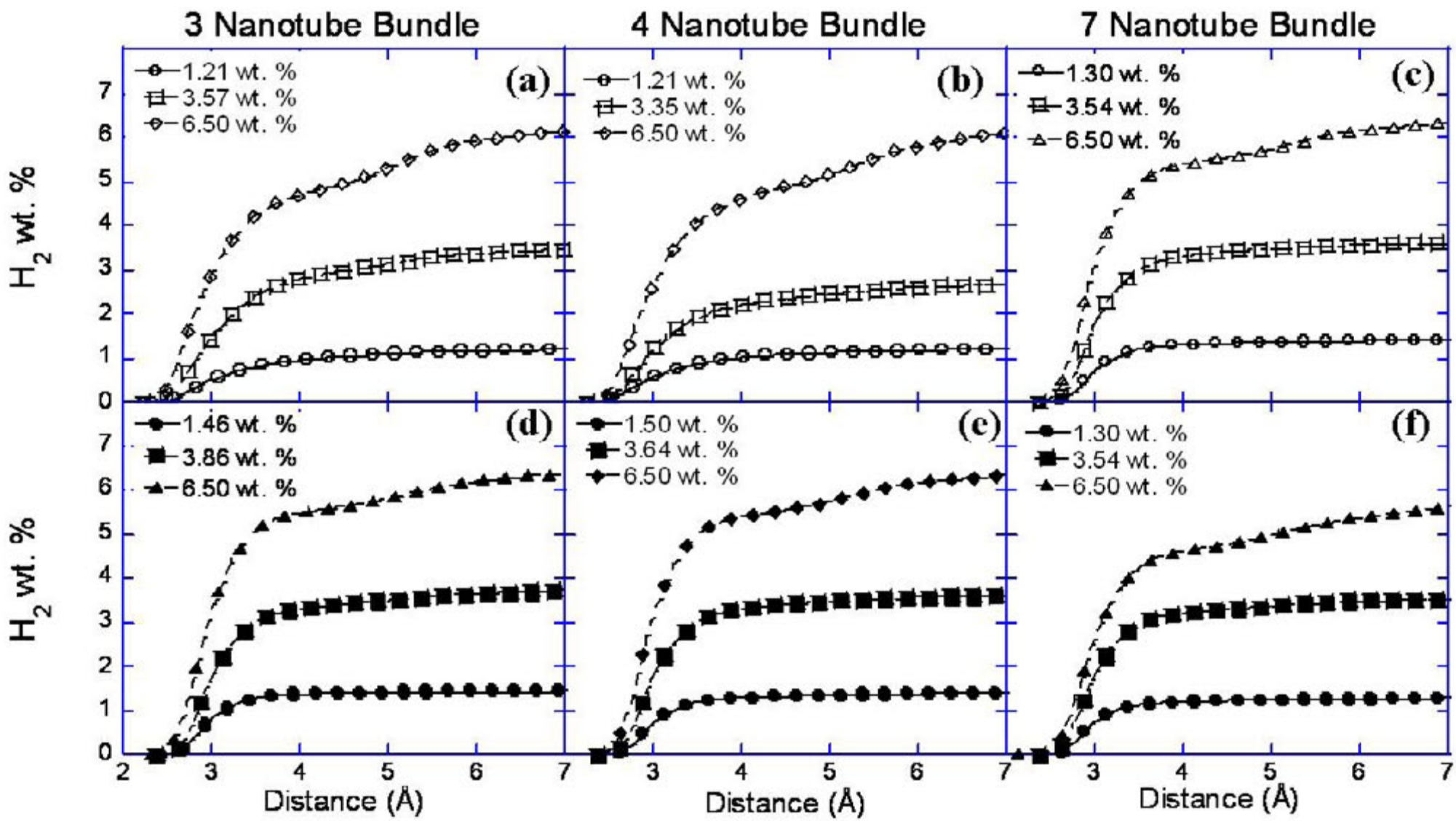
$$n(r) = \int_0^r A(r')dr'$$

$$\varepsilon'_{gas}(r) = \left(\varepsilon_{gas} - \frac{\varepsilon_{sys} - \varepsilon_{sub}}{N}\right)\frac{n(r)}{N} + \frac{\varepsilon_{sys} - \varepsilon_{sub}}{N}$$

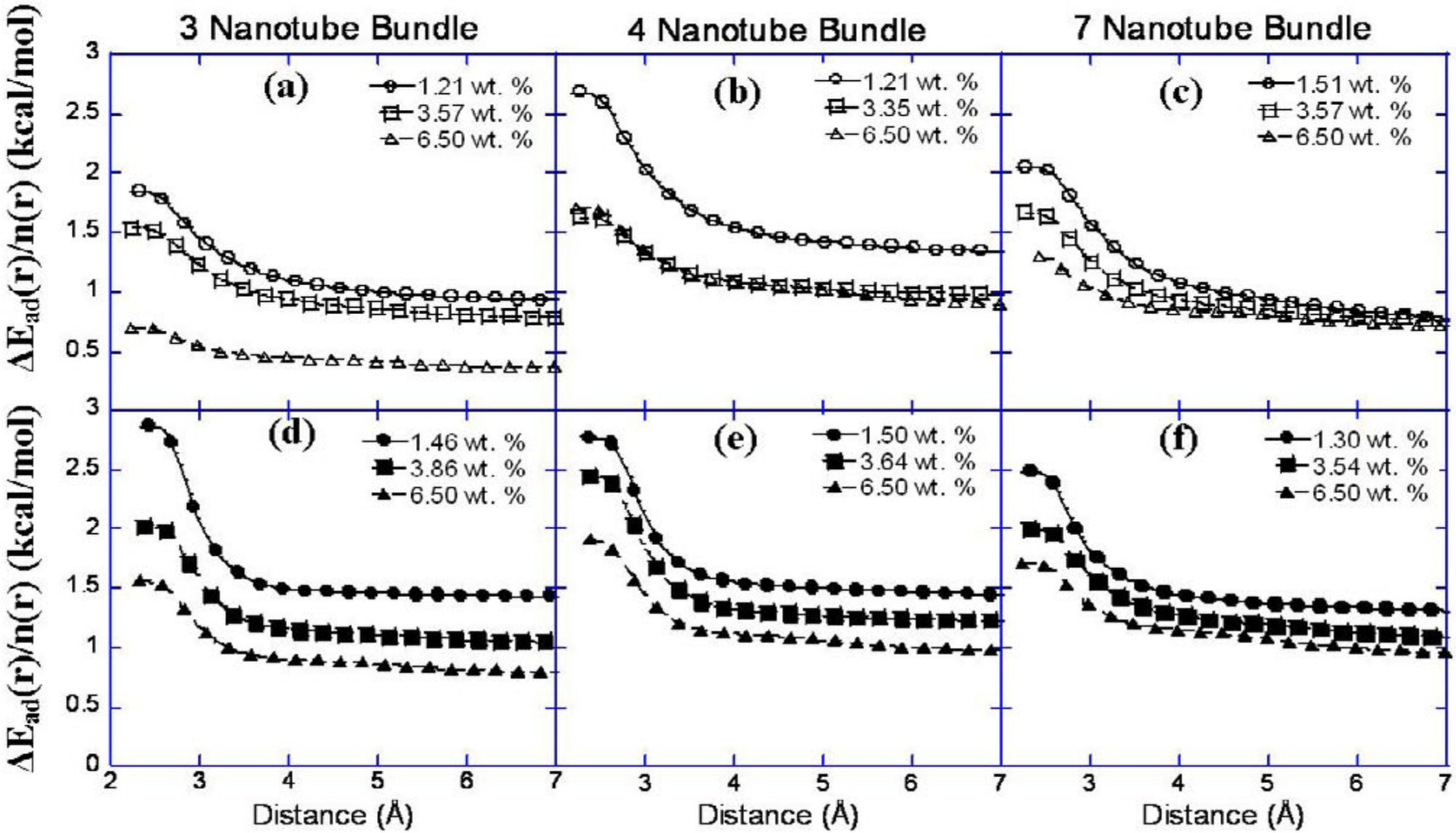
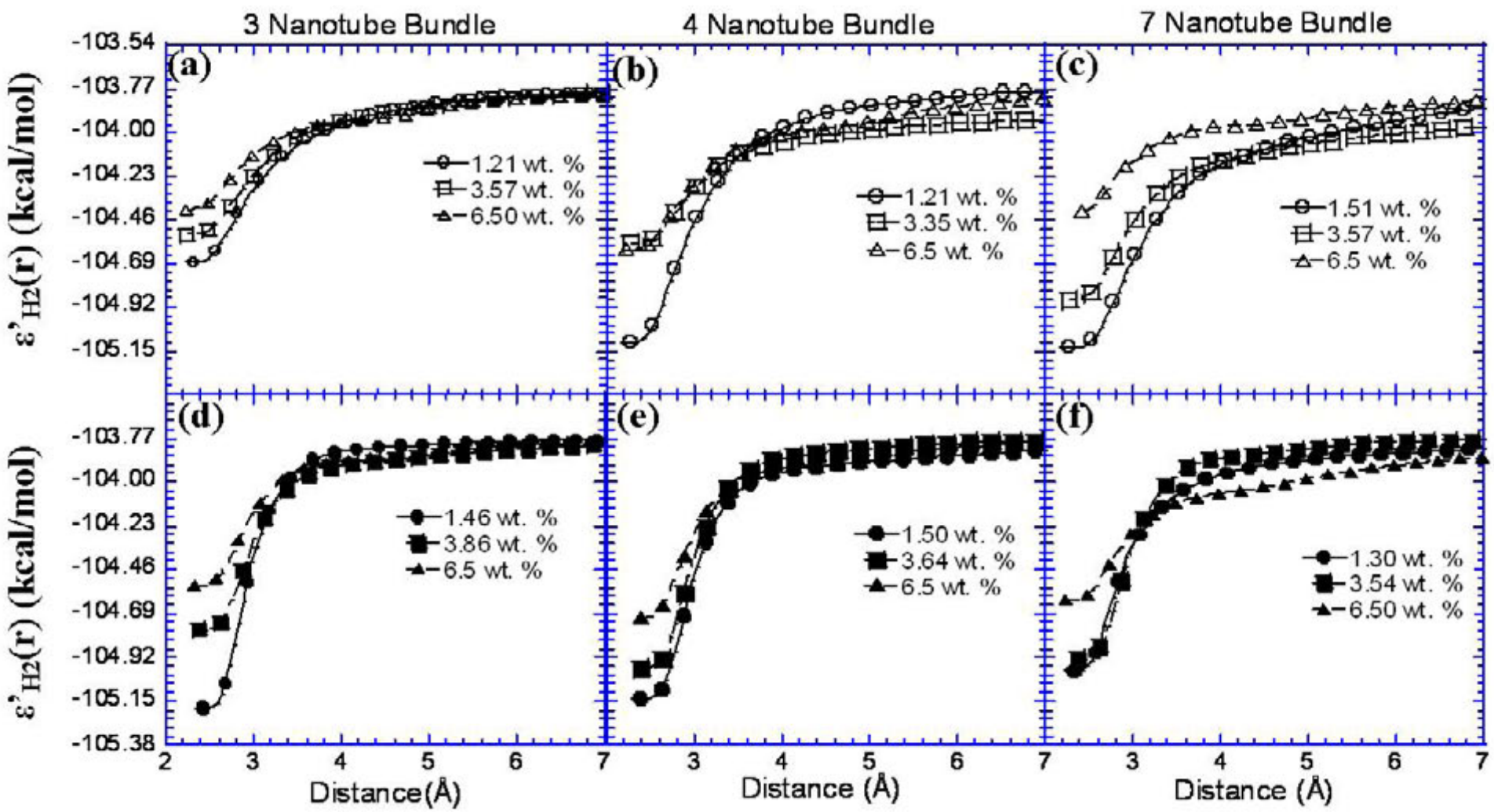
$$\varepsilon_{gas} \le \varepsilon'_{gas}(r) \le \frac{\varepsilon_{sys} - \varepsilon_{sub}}{N}$$

$$\Delta E_{ad}(r) \to \begin{cases} 0, & r \to 0 \\ N\varepsilon_{gas} + \varepsilon_{sub} - \varepsilon_{sys}, & r \to \infty \end{cases}$$

Reference: Adsorption Capacity



Reference: Adsorption Energy



Reference: H_2 Interaction Energy vs. Distance from Adsorbent (ε')