### Adsorption at the Nanoscale: A New Frontier in Fundamental Science and Applications



September 22-24, 2011 University of Missouri Columbia, Missouri

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Hiden Isochema Advancing Sorption Analysis



Characterizing Porous Materials and Powders



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### **Conference Organizers**

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### **Conference Coordination and Support:**

Ms. Barbara Wills, MU Conference Office

### **Adsorption at the Nanoscale - Program**

### Thursday Sept. 22 (Monsanto Auditorium, Life Sciences Center)

8:00	8:15	Shuttle Service from Hampton Inn to LSC (or walk 10-15 min)			
8:00	9:00	Registration (entrance to Monsanto Auditorium, LSC)			
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9:45	pg. 6	The Quantum Excitation Spectrum of Adsorbed Hydrogen	R. Olsen	U. of Missouri	
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11:45	pg. 9	The Effect of Many-Body Interactions on the Physical Adsorption on Carbon-based Systems	HY. Kim	Southeastern Louisiana U.	
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1:30	pg. 11	Gas adsorption on carbon nanostructures	A. Migone	Southern Illinois U.	
2:00	pg. 12	Adsorption of helium clusters on graphene	L. Vranjes Markic	U. Split	
2:30	pg. 13	Influence of edges on adsorption in nanopores with finite pore walls from truncated graphene	L. Firlej	Université Montpellier 2	
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4:30	pg. 15	Experimental Challenges in the Determination of Gas Adsorption by Nanoporous Media at Elevated Pressures	D. Broom	Hiden Isochema	
5:00	pg. 16	Sorption, Pore Condensation and Hysteresis Behavior in Advanced Nanoporus Silica and Carbon Materials	M. Thommes	Quantachrome	
5:30	7:00	Posters, and visit to Physics & Astronomy Labs (details TBA)			
7:00	8:30	Dinner (McQuinn Atrium, LSC)			
8:45	9:00	Shuttle Service from LSC to Hampton Inn (or walk 10-15 min)			

### Adsorption at the Nanoscale - Program

### Friday, Sept. 23 (Monsanto Auditorium, Life Sciences Center)

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### **Adsorption at the Nanoscale - Program**

### Saturday, Sept. 24 (Jesse Wrench Auditorium, Memorial Union)

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		n X Chair: F. Ancilotto, Padova		
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### Study of water diffusion on single-supported bilayer lipid membranes by quasielastic neutron scattering

M. Bai<sup>1</sup>, A. Miskowiec<sup>1</sup>, F. Y. Hansen<sup>1</sup>, <u>H. Taub</u><sup>1</sup>, T. Jenkins<sup>2</sup>, M. Tyagi<sup>2,3</sup>, D. A. Neumann<sup>2</sup>, S. O. Diallo<sup>4</sup>, E. Mamontov<sup>4</sup>, K. W. Herwig<sup>4</sup>, and S.-K. Wang<sup>1</sup>

High-energy-resolution quasielastic neutron scattering has been used to elucidate the diffusion of water molecules in proximity to single bilayer lipid membranes (DMPC) supported on a silicon substrate. The structure of our samples was first characterized using Atomic Force Microscopy as a function of temperature. We then performed high-energy-resolution quasielastic neutron scattering experiments at the NIST Center for Neutron Research and the Spallation Neutron Source at Oak Ridge National Laboratory on similarly prepared samples. By varying both membrane temperature and level of hydration, we identify three different types of diffusive motion of the water molecules: bulk-like, confined, and bound. The motion of bulk-like and confined water is fast compared to that of the water molecules bound to the lipid head groups, which appear to move on the same nanosecond time scale as the lipid molecule center-of-mass. Intensity analysis of the guasielastic scattering from this slower motion yields about nine water molecules bound per lipid in reasonable agreement with NMR experiments on multilamellar DMPC samples. The relation of these experimental results with molecular dynamics simulations on a freestanding DMPC membrane at a temperature of 303 K will be discussed.

<sup>&</sup>lt;sup>1</sup>Department of Physics and Astronomy and University of Missouri Research Reactor, University of Missouri, Columbia, Missouri

<sup>&</sup>lt;sup>2</sup>Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD

<sup>&</sup>lt;sup>3</sup>Department of Materials Science and Engineering, University of Maryland, College Park, MD

<sup>&</sup>lt;sup>4</sup>Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN

#### The Quantum Excitation Spectrum of Adsorbed Hydrogen

Raina J. Olsen, Matthew Beckner, Matthew B. Stone, Peter Pfeifer, Haskell Taub, and Carlos Wexler

Department of Physics and Astronomy; University of Missouri, Columbia, MO

Inelastic neutron scattering is used to study the quantum excitation spectrum of molecular hydrogen adsorbed on carbon. We show that there exist two distinct types of excitation which are either bound or mobile with respect to their translational motion parallel to the adsorption plane. We utilize the dependence of various excitations on the direction of neutron momentum transfer to demonstrate strong coupling between internal and external degrees of freedom. Based on the experimental evidence, we present models for the stationary states of adsorbed hydrogen in which the corrugation of the adsorption potential results in a mixing of free rotor states such that molecules perform a rocking motion as Separation of experimental spectra into these two types of they diffuse. excitations provides a new qualitative measurement of the nanoscale planarity of the adsorption surface. Future theoretical work with more accurate models for the stationary states may lead to new quantitative characterization methods in this regime. Our results are also particularly applicable to room temperature hydrogen adsorption because neutrons with thermal incident energies are used and the excitations probed are preferentially occupied at room temperature. Previous theoretical treatments of adsorption have been primarily classical and we briefly discuss how our results may be used to develop more accurate quantum models.

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#### Open Carbon Frameworks (OPF) – new hypothetical structures for hydrogen storage

B. Kuchta<sup>1,2</sup>, L. Firlej<sup>1,3</sup>, and P.Pfeifer<sup>1</sup>

<sup>1</sup>Department of Physics and Astronomy, University of Missouri, Columbia, MO, USA <sup>2</sup>Laboratoire Chimie Provence, Aix-Marseille University, Marseille, France

<sup>3</sup>Laboratoire Charles Coulombs, Université Montpellier 2, Montpellier, France

In recent years, a great emphasis has been placed on replacing fossil fuels



Fig.1 New structures of Open Carbon Framework (OCF)

with clean, renewable energy for use in vehicles. One potential solution is the use of hydrogen gas as a fuel source to power a fuel cell. For vehicular use, the US Department of Energy

(DOE) has identified three major challenges to implementing a hydrogenpowered solution: (i) hydrogen production costs must be substantially lowered, (ii) a substantial reduction in fuel-cell costs, (iii) and hydrogen storage systems capable of delivering a driving range of hundreds of kilometers, without major detrimental effects to vehicle cost, safety, or cargo capacity must be developed. Mechanism of hydrogen adsorption in carbon porous structures is a fundamental problem for these applications. There exist many carbon porous structures which exhibit different capacities of adsorbed hydrogen, practically, all of them too low for practical applications.

It can be shown that it is not possible to increase hydrogen storage capacity only by modification of slit geometry without simultaneous increase of the specific surface. So, we have introduced structures with higher surfaces and analyzed their adsorption properties. These new models of hypothetical structures represent ordered carbon structure with low density architecture required for effective application of porous carbons for mobile storage. We call them Open Carbon Frameworks (OCF). Theoretically they may have the specific surfaces exceeding  $6000 \text{ m}^2/\text{g}$ .

### Modeling the dynamics of capillary condensation and evaporation processes

#### Peter A. Monson

Department of Chemical Engineering, University of Massachusetts, Amherst, MA

Fluids confined in mesoporous materials exhibit behavior reminiscent of phase transitions in the bulk (e.g. vapor to liquid condensation) but modified by confinement. In addition hysteresis can occur between adsorption and desorption, an indication of failure by the system to reach thermodynamic equilibrium during condensation and/or evaporation processes. Understanding these phenomena requires consideration from both thermodynamic and dynamic perspectives.

Recent years have seen dramatic progress in the modeling the thermodynamics of adsorption and desorption for fluids in mesoporous materials based on density functional theories. In this presentation we discuss an approach to modeling the relaxation dynamics that is consistent with the thermodynamic picture from density functional theory. We discuss the application of this dynamical theory to fluids in simple pore geometries and pore networks. In addition to providing quantitative information about the adsorption/desorption dynamics, the theory also yields visualizations of condensation and evaporation processes associated with the filling and emptying of porous materials by fluids.

### The Effect of Many-Body Interactions on the Physical Adsorption on Carbon-based Systems

#### Hye-Young Kim

Department of Chemistry and Physics; Southeastern Louisiana University; Hammond, LA

The practice of adopting empirical, pair-wise potentials to describe the gas-gas and gas-surface interactions in physical adsorption is the basis for much of computational material science. While it is a widely accepted practice and is inevitable most of the time, it is very difficult to provide justification for using the sum of pair-wise potentials to describe the evidently many-body interactions that are sensitive to the electronic properties of the gas atoms/molecules and surface.

The search for reliable empirical potentials has been, still is, and will be one of the major challenges in computational material science. A familiarity with the current understanding of the effect of many-body interactions and the limits of the prevailingly available pair-wise potentials will certainly help in making an intelligent choice of potentials and in discussing experimental or simulation results using a particular set of potentials. Limiting consideration to simple gas atoms adsorbed on various carbon-based systems, this talk will provide background, summarize current understanding, and discuss key issues in the effect of many-body interactions on physical adsorption.

### Overview of the U.S. DOE Hydrogen Storage Program's Efforts in Adsorption Materials and Systems

<sup>1,3</sup>Scott McWhorter, <sup>1</sup>Grace Ordaz, <sup>2</sup>Jesse Adams and <sup>1</sup>Ned Stetson

<sup>1</sup>Fuel Cell Technologies Program, U.S. Department of Energy (U.S. DOE), Washington, DC

<sup>2</sup>Fuel Cell Technologies Program, U.S. Department of Energy (U.S. DOE) – Golden Field Office, Golden, CO

<sup>3</sup>Analytical Development Directorate, Savannah River National Laboratory, Aiken, SC

The U.S. DOE Hydrogen Program's mission is to reduce oil use and green house gas emissions in the U.S. transportation sector and to enable clean, reliable energy for early market fuel cell applications such as stationary and portable power generation. The requirements for hydrogen storage on-board vehicles and in early market applications continue to be one of the most technically challenging barriers to the widespread commercialization of hydrogen fuel cells. The DOE-EERE hydrogen storage activity primarily focuses on applied research and development of materials and engineering to provide low-pressure systems that meets packaging, cost, safety and performance requirements competitive with current technologies.

This presentation summarizes the current DOE-EERE Hydrogen Storage R&D program status, as well as on-going and planned future activities. The discussion will include a summary of hydrogen storage R&D activities related to hydrogen sorbents, that includes both material and system level efforts. Additionally, progress from the Hydrogen Storage Engineering Center of Excellence towards designing a cryo-sorbent based system will be presented. Finally, initiatives and opportunities to address storage R&D needs to facilitate the EERE Fuel Cell Technologies Program's objectives for deployment and market growth of fuel cell systems for early market applications will be discussed.

### **Gas Adsorption on Carbon Nanostructures**

#### Aldo D. Migone

Southern Illinois University Carbondale, Carbondale, Illinois

The results of a series of studies conducted to explore the adsorption behavior of linear hydrocarbon chains on bundles of carbon nanotubes will be discussed in this talk.

The equilibrium characteristics of films of ethane, propane, butane and ethylene adsorbed on the surface of bundles of close-ended single-walled carbon nanotubes will be presented. For each species we will present: a set of adsorption isotherms; the evolution of the adsorbate's isosteric heat as a function of fractional coverage; and the values of the binding energy for the strongest binding sites present in the bundles.

We will compare how the monolayer isotherm features evolve between the various systems as a function of the length of the hydrocarbon adsorbate; and, we will also discuss how the effective surface areas measured using a sequence of linear hydrocarbons vary with adsorbate chain length.

Results will be presented that describe how the approach to equilibrium for points along an isotherm vary with fractional coverage. We will show how this behavior evolves as a function of hydrocarbon chain length by comparing results obtained for alkanes from ethane to pentane.

This research was supported by the NSF through grant # DMR-0705077

#### Adsorption of helium clusters on grapheme

L. Vranješ Markić<sup>1</sup>, I. Bešlić<sup>1</sup>, P. Stipanović<sup>1</sup>, R. E. Zillich<sup>2</sup>

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<sup>2</sup>Institute for Theoretical Physics, Johannes Kepler Universität, Linz, Austria

We report the results of the study of  ${}^{4}\text{He}_{N}$  clusters adsorbed on one and both sides of a graphene sheet. Interactions of  ${}^{4}\text{He}$  clusters with graphene are modelled using an averaged helium-carbon potential that depends only on the distance to the graphene sheet, and a potential constructed as a sum of individual helium-carbon interactions. That way, we assess the effect of corrugation on the binding properties of helium clusters, both using isotropic and anisotropic helium-carbon interactions. In addition, we assess the influence of the substrate-mediated McLachlan interaction.

All the calculations have been performed using quantum Monte Carlo methods. At zero temperature the ground-state properties of  ${}^{4}\text{He}_{N}$  for 2  $\leq$  N  $\leq$  50 have been determined using variational and diffusion Monte Carlo calculations. We find that clusters adsorbed on both sides of graphene are correlated. In addition, we observe the changes in the size of the clusters. For selected larger clusters, calculations have been performed also at finite temperature by path integral Monte Carlo simulations.

#### Influence of edges on adsorption in nanopores with finite pore walls from truncated graphene

L. Firlej<sup>1,3</sup>, J.Jagiello<sup>4</sup>, B. Kuchta<sup>1,2</sup>, J.Romanos<sup>1</sup>, M. Beckner<sup>1</sup> and P.Pfeifer<sup>1</sup>

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<sup>3</sup>Laboratoire Charles Coulombs, Université Montpellier 2, Montpellier, France

<sup>4</sup> Micromeritics Instrument Corporation, Norcross, Georgia

Adsorption mechanism depends on adsorbent geometry. The most important factors defined by geometry are: the surface accessible for adsorption and the



Fig1.Upper:Components of adsorption in finite pore (R=1.42nm. H=0.7nm). Down: density distribution of the adsorbed  $N_2$  molecules in the same pore.

distribution of energy of adsorption. In a particular type of pores with walls built from graphene layer fragments, we observe a competition between these two factors: an increase of adsorption due to the additional adsorption surface introduced by the walls' edges and a decrease of adsorption uptake due to smaller adsorption energy near the edges.

We present the results of Monte Carlo simulations of  $N_2$  and  $H_2$  adsorption in model, finite size

carbon slit pores. This model mimics real carbon samples better than usually used infinite pore models, whatever is the assumed pore shape (slit-like, tubular, curved etc). In particular, it allows us to account for the adsorption at the pore edges, totally neglected in infinite models. We show that the contribution of edges to the total adsorption is not negligible: in smallest pores, with the diameters comparable with the pore width, the edge contribution can be even equally or more important than that of the pore inside. We discuss and compare Monte Carlo simulations and DFT approach in similar pore geometries.

### Characterization of nanoporous materials using 2D-NLDFT finite pore models

#### Jacek Jagiello, Jeffrey Kenvin, James P. Olivier

#### Micromeritics Instrument Corporation, Norcross, GA

Accurate description of the pore structure of microporous carbons is important for their traditional applications such as gas separation or the removal of atmospheric pollutants as well as for the most advanced applications such as the development of electrical double layer capacitors (EDLC).

The most commonly used carbon pore model is a slit shape pore infinitely extended in two dimensions. This model allows describing gas adsorption isotherms as a function of temperature, pressure and pore width. A set of theoretical isotherms (kernel) calculated using tools such as the non-local density functional theory (NLDFT) or Monte Carlo simulations can be used for the characterization of carbon pore structure in terms of its pore size distribution (PSD).

To describe adsorption in the model pores we apply the Tarazona's version of NLDFT. The solid-fluid interaction potentials are calculated by the numerical integration of the LJ potential over the pore walls. Recently, we have proposed using a finite pore model for the carbon PSD analysis [1]. In that model, we assumed the simplest possible finite slit pore having parallel circular graphene walls. In present work, we consider models with slit pore geometries as well as pores with curved walls. In finite slit pores the graphene walls are finite in x and infinite in y directions. These pores may be open on both sides of the strip walls or partially closed on one side of the pore by a perpendicularly oriented graphene sheet. The latter pores may occur as a result of crossing between the graphite-like crystallites.



Recent advances in synthesis of porous carbons in confined geometry of zeolites or other porous materials produced carbons with new structural features. Carbon replicas obtained from zeolites may include curved graphene like structures. We consider several types of pores created by curved graphene surfaces. As an example, in Fig 1 we show the N<sub>2</sub>

density profile in a short cylindrical pore (ring) with curved walls.

Fig 1. Calculated-cross sectional density profile of N<sub>2</sub> adsorption in a short cylinder (ring) with curved walls. [1] J. Jagiello, J. P. Olivier, *J. Phys. Chem. C* **113**, 19382-19385 (2009)

### Experimental challenges in the determination of gas adsorption by nanoporous materials at elevated pressures

#### D. P. Broom

Hiden Isochema Ltd; Warrington, UK

The measurement of the adsorption of gases by nanoporous materials at above ambient pressure is important for a range of practical gas adsorption-based applications, including the adsorptive storage of energy gases, such as hydrogen and methane, and gas separation technology. However, the experimental determination of the amount of gas adsorbed by nanoporous materials, at an elevated pressure, is complicated by the increase in the significance of the errors involved in macroscopic gas adsorption measurement as the density of the gas phase increases, a dependence that affects both the manometric and gravimetric measurement of adsorption. In addition, as the external gas pressure increases, the difference between the excess and absolute adsorbed quantities also becomes more significant.

In this presentation, the errors involved in the measurement of the adsorption of gases at elevated pressures are therefore discussed, together with the implications of the choice of method used for the conversion of the excess to the absolute adsorption. The error sources include those associated with our knowledge and understanding of the volume or density of real nanoporous materials, in which the geometry of the pores and the surface structure can begin to significantly affect the volume accessible to different size molecules, relative to the total skeletal volume of the solid, and the accuracy of the description of the compressibility of a real gas. The equivalence of the dead volume and buoyancy effect corrections required for the manometric and gravimetric techniques, respectively, will also be discussed with a view to identifying the importance of each correction type to the accuracy of adsorption measurements performed at elevated pressures.

### Sorption, Pore Condensation and Hysteresis Behavior in Advanced Nonporous Silica and Carbon Materials

#### Matthias Thommes

Quantachrome Corporation, Boynton Beach, FL

A comprehensive textural characterization of novel nanoporous materials has become more important than ever for the optimization of novel systems used in many important existing and potentially new applications. The most popular method to obtain surface area, pore size, pore size distribution and porosity information from powders and porous solids is gas adsorption. However, despite the recent progress achieved in the understanding of the adsorption mechanism of fluids in highly ordered micro-and mesoporous molecular sieves with simple pore geometries (e.g., M41S materials), there are still many open questions concerning the surface and textural characterization of more complex porous For instance, fluids adsorbed in hierarchically structured microsystems. mesoporous materials can exhibit very complex, but very interesting pore condensation and hysteresis behavior. A combination of phenomena such as delayed pore condensation, pore blocking/percolation and cavitation induced evaporation can be observed, which is reflected in characteristic types of adsorption hysteresis. Sorption hysteresis introduces of course a considerable complication for pore size analysis by physical adsorption, but if interpreted correctly, provides important information about the pore structure/network.

#### Materials Challenges Facing Adsorption Based Onboard H2 Storage

#### Mei Cai and Anne Dailly

Chemical Sciences and Materials Systems Laboratory; General Motors Research and Development Center; Warren, MI

The development of PEM fuel cell/hydrogen propulsion technology has generated significant materials challenges for the scientific and engineering communities. Among them, the discovery of a best material in which hydrogen can be stored in its molecular or atomic form for vehicular application is a formidable challenge. To date, various adsorbents such as zeolites, different types of carbon (including activated carbons and nanotubes), and more recently Metal-Organic Frameworks (MOFs) have been explored as potential hydrogen storage materials. This presentation reviews some recent research and development activities that focused on adsorption based hydrogen storage technologies conducted at General Motors. The current status of this technology will be described as is the expected future capability and performance of the critical elements in a valid hydrogen storage system for vehicular application.

### Nanospace-Engineered Carbons for Reversible On-Board Storage of Natural Gas and Hydrogen

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An overview is given of the development of advanced nanoporous carbons at the University of Missouri as storage materials for natural gas (methane) and molecular hydrogen in on-board fuel tanks for next-generation clean automobiles. High specific surface areas, porosities, and sub-nm/supra-nm pore volumes are quantitatively selected by controlling the degree of carbon consumption and metallic potassium intercalation into the carbon lattice during the activation process. Tunable bimodal pore-size distributions of sub-nm and supra-nm pores are established by subcritical nitrogen adsorption, small-angle x-ray scattering, and transmission electron microscopy. Optimal pore structures for gravimetric and volumetric gas storage, respectively, are presented. We present an experimental study of the prediction that substitution of surface carbon with boron ("boron doping") increases the binding energy for hydrogen and, therefore, enhances hydrogen adsorption (electron donation from H<sub>2</sub> to electron-deficient boron). Microscopic Fourier transform infrared spectroscopy establishes the presence of B-C bonds. A sample with 8 wt% boron exhibits a 30% increase in excess adsorption per surface area at 303 K and 200 bar, relative to the undoped parent material. Methane and hydrogen adsorption isotherms up to 250 bar on monolithic and powdered activated carbons are reported and validated, using several gravimetric and volumetric instruments. Current best gravimetric and volumetric storage capacities are: 256 g CH<sub>4</sub>/kg carbon and 132 g  $CH_4$ /liter carbon at 293 K and 35 bar; 26, 44, and 107 g H<sub>2</sub>/kg carbon at 303, 194, and 77 K respectively and 100 bar. Adsorbed film density, specific surface area, and methane binding energy are analyzed separately using the Clausius-Clapeyron equation, Langmuir model, and lattice gas models. A prototype 10-liter hydrogen adsorbent tank, loaded with 7 kg of optimized carbon, is described to measure hydrogen storage and delivery under conditions similar to an on-board tank.

### Adsorption storage of hydrogen: from materials properties to system design

#### R. Chahine

Institut de recherche sur l'hydrogène, Université du Québec a Trois-Rivières

R&D efforts are being pursued to improve the efficiency and economics of onboard hydrogen storage systems for mobile applications. Hydrogen storage via physisorption on porous materials, such as activated carbon, carbon nanostructures and metal organic frameworks (MOFs) is particularly enticing due to its inherent reversibility and cyclability. Moreover, these materials exhibit fast kinetics and can operate at relatively low storage pressures. However, due to the low binding energy, acceptable densities are only attainable at cryogenic temperatures.

We will present the results of our evaluation of an adsorption-based hydrogen storage tank for vehicular application. We will discuss the net storage capacity of the system over wide temperature and pressure ranges and compare it with other hydrogen storage methods.

### Functionalized nanoporous sorbents: From entrance effects to reactive centers

J. Karl Johnson, Jinchen Liu, De-Li Chen, and Pabitra Choudhury

Department of Chemical & Petroleum Engineering; University of Pittsburgh; Pittsburgh, PA

Many adsorption simulations probe only the equilibrium properties of a sorbent. This is often sufficient and adsorption selectivity can be a useful component in theories for predicting the performance of membranes. However, in situations where entrance effects dominate equilibrium calculations can be misleading. We present simulations of nanoporous materials where entrance effects cannot be ignored. We use molecular dynamics approaches to study entrance effects for pure and mixed gases in metal organic frameworks and porous carbon nanotubes. We complement our classical simulations with electronic structure density functional theory to compute the energetics of entrance effects. We also consider porous materials that can act as catalysts. We consider doped carbon nanotubes as a model system and show how dopants can act both as reactants and catalysts. We consider the role of defects on the nanotube in the reactions. We also examine metal organic framework materials that are chemically reactive.

### Structure and dynamics of fluids at patterned substrates

#### S. Dietrich

Max-Planck-Institute for Intelligent Systems, Stuttgart, Germany Institute for Theoretical and Applied Physics, University of Stuttgart, Stuttgart, Germany

The morphologies of equilibrated wetting films on geometrically structured substrates are studied by density-functional-based effective interface models. For specific examples these results are compared with X-ray scattering data. The wetting behaviour of responsive substrates is discussed with a view on liquid films in contact with hair-like structures on leaves. The motion of nanodroplets near geometrical or chemical steps is analyzed theoretically.

### Adsorption of fluids on nanostructured substrates from atomistic simulations

Francesco Ancilotto, Pierluigi Silvestrelli, Francesca Costanzo and Flavio Toigo

Dipartimento di Fisica "G.Galilei" - Universita' di Padova (Padova) and CNR-IOM-Democritos National Simulation Center (Trieste) Italy

I will illustrate some recent applications of computational methods (based on semi-empirical and "ab initio" Density Functional theory, and Grand Canonical Monte Carlo techniques) to the adsorption of classical and quantum fluids on substrates that are structured at the nanoscale. In particular I will discuss the importance of "ab initio" electronic structure calculations to compute the van der Waals contribution to the adatom-surface interactions.

In studying physical adsorption, computation of reliable physisorption potentials is difficult because of the small energy scale involved. To avoid this problem, the majority of simulation calculations are based on semiempirical potentials, e.g. combining rules. "Ab initio" methods are not necessarily reliable because of the fundamental role of nonlocal correlation in van der Waals (VdW) interactions, complicating the applicability of Density Functional theory based methods.

We have recently developed in our group a novel scheme in which VdW effects can be efficiently evaluated using the notion of maximally-localized Wannier functions (MLWF). The coefficients that describe the long-range interaction between two separated fragments of matter can thus be calculated directly from the basic information (center positions and spreads) given by the MLFWs. Once an accurate interaction potential for atoms and molecules interacting with a planar surface is known, relatively simple numerical methods can be employed to determine the adsorption potential for atoms and molecules interacting with nonplanar substrates characterized by an arbitrary surface topology, like cavities, wedges, pores, etc.

### Spectroscopic studies of small molecules in Metal Organic Framework (MOF) materials

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Hydrogen storage and  $CO_2$  separation are two of the most challenging problems for the use of renewable energy sources and to reduce  $CO_2$  emission. Metalorganic Frameworks are promising candidates for hydrogen storage and  $CO_2$ separation because their high surface area and porosity along with their tailorable structures facilitate high hydrogen and  $CO_2$  physisorption on specific sites of the structures.

This work explores the incorporation of hydrogen and CO<sub>2</sub> into various MOFs using infrared (IR) and Raman spectroscopy to characterize their interaction. IR spectroscopy can distinguish possible H<sub>2</sub> binding sites based on the perturbation of the internal H<sub>2</sub> stretch mode. Comparative IR measurements are performed on saturated metal center MOFs and on unsaturated metal center MOF-74-M (M=Zn, Mg and Ni) by varying the ligand and/or the metal center. We combine the experimental IR measurements and theoretical van der Waals density functional (vdW-DF) calculations to derive quantitative information from the vibrational band shifts and dipole moment strengths.

In addition to  $H_2$ , we have explored  $CO_2$  adsorption and selectivity in a flexible MOF system using Raman and IR spectroscopy. The  $CO_2$  specific interaction with the framework and the specific connectivity of the metal to the ligands is found to be the main reasons for this MOFs flexibility leading to its large  $CO_2$  selectivity.

The sensitivity of IR and Raman spectroscopy to weak interactions of small molecules with MOFs makes it possible to understand the effect of each building block of these frameworks on these weak interactions.

#### Thermodynamics and Kinetics of Nano-cluster and Nanoconfined Complex Hydrides

#### E. H. Majzoub

Center for Nanoscience and Department of Physics and Astronomy; University of Missouri, St. Louis

The equilibrium plateau pressure of a metal hydride at a given temperature is a characteristic thermodynamic quantity, and determines the application and engineering required for a hydrogen storage system. While recent interest has focused on complex metal hydrides such as NaAlH<sub>4</sub> and Ca(BH<sub>4</sub>)<sub>2</sub>, these compounds are not as easily tunable as the interstitial metallic hydrides through alloying with other metal atoms, due to the strongly ionic character of the cohesive energy. However, the complex hydrides are superior on a wt.% hydrogen basis, and are the preferred materials for vehicular transport. In order to address thermodynamic tunability, we investigate these materials at the nanoscale, where the ratio of surface to bulk atoms impacts the energetics. Recent theoretical work indicates that small clusters of MgH<sub>2</sub>, for example, can significantly lower the desorption enthalpy with respect to bulk. Small metal or hydride clusters may be incorporated into nanoporous frameworks such as metal organic frameworks (MOFS), block co-polymer (BCP) templates, or nanoporous hard carbons, for example, to prevent agglomeration and perhaps even improve tunability through particle/surface interactions. We present theoretical results for desorption energetics of free nanoclusters of NaAlH<sub>4</sub> as a function of temperature and pressure. Prototype geometries for the clusters were generated using a well-validated electrostatic ground state approach to a global optimization of the cluster total energy using a recently developed non-conventional Monte Carlo random walk in energy space. First-principles density functional theory applied to the prototype clusters was used for full free energy calculations of the clusters and decomposition products. Results will be discussed with relation to recent experimental work on incorporation of complex hydrides in nanoporous framework materials, and the importance of the surface chemistry of the frameworks.

### Hydrogen storage in metal-organic frameworks via spillover and gate-opening mechanism

<u>Angela D. Lueking</u>, Xiaoming Liu, Sarmishtha Sircar, Cheng-Yu Wang, Qixiu Li The Pennsylvania State University, University Park, Pennsylvania USA

We are currently exploring novel trapping mechanisms for gas storage and separations, using a collaborative combination of experiment and theory. In one study, we are looking at how carbon materials may be engineered to trap molecular hydrogen in tightly knit micropores, through catalyst addition (i.e. hydrogen spillover), penetration under extreme pressures, and polymerization of polyaromatic hydrocarbons in the presence of molecular hydrogen. In the former, we are utilizing high-pressure in situ characterization techniques to identify the mechanism by which reversible hydrogenation of the carbon substrate is possible. In the two latter cases, we believe hydrogen loading under extreme conditions may lead to diffusion-limited hydrogen evolution from the materials, after simultaneous hydrogenation and carbon restructuring. In a second study, we are exploring the kinetics of the novel 'gate-opening' (GO) phenomenon that has emerged for metal-Organic Frameworks (MOFs) materials. GO is typically characterized by an unusual S-shaped isotherm that is thought to be due to activation of a thermodynamic switch at a particular temperature and pressure that opens the structure, allowing for a significant increase in porosity. The GO phenomenon remains poorly understood and relatively unexplored in terms of classic and emerging gas separations. In our laboratory, we have demonstrated that the gas-surface interaction dictates the rate of diffusion into the material, and this can be harnessed for kinetic separations. The two studies taken as a whole describe the diffusion-limited evolution of gases, representing a shift from 'traditional' solid state adsorbents with thermodynamic limitations to a regime that is limited by chemical kinetics. In this talk, I will discuss the original 'inspiration' behind our work in trapping, our recent use of in situ spectroscopic techniques to identify active adsorption sites, the kinetics of gas trapping, and then propose a means by which to utilize these phenomenon in gas storage and separations.

### Selective adsorption of CO<sub>2</sub> in microporous metal organic framework (MMOF) materials

#### Zhijuan Zhang, Haohan Wu, Jing Li

Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ

As global warming is becoming one of the most pressing issues worldwide, it is imperative to develop effective ways to significantly reduce the emission of carbon dioxide and other greenhouse gases. Adsorption-based separation methods have the advantage of easy control and low energy demand. However, to make such a process practical, it is essential to develop low-cost adsorbents of high selectivity and capacity for  $CO_2$ , especially at relatively low pressures (e.g.~0.1-0.15 atm, the partial pressure of  $CO_2$  in flue gases). This talk will focus on the synthesis and functionalization of different types of microporous metal organic framework (MMOF) materials, their selective adsorption of  $CO_2$  and their potential for use in adsorption based CCS.

#### Phase Behavior of Ar and Kr Films on Carbon Nanotubes

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<sup>d</sup> Physics Department, Penn State University, University Park, PA

Recent experiments (Wang et al., 2010) have found evidence of phase transitions of gases adsorbed on a single carbon nanotube. In order to understand the observations, we have carried out classical grand canonical Monte Carlo simulations of this system, for the cases of Ar and Kr on zigzag and armchair nanotubes with radius R > 0.7 nm. The calculated behavior resembles the experimental results in the case of Ar. However, the prominent, ordered phase found for Kr in both simulations and (classical) energy minimization calculations differs from that deduced from the experimental data. A tentative explanation of the apparent discrepancy is that the experiments involve a nanotube of rather large radius (>1.5 nm).

### Conductance isotherms for adsorption on individual singlewalled carbon nanotubes

D.H. Cobden, H.C. Lee, B. Dzyubenko, and O.E. Vilches

Department of Physics, University of Washington, Seattle WA

The ability to make transistors from suspended carbon nanotubes allows one to probe the interaction of adsorbed atoms and molecules with the carbon substrate electrons. We have studied the effects of adsorbing noble gases on the electrical properties of individual single-walled nanotubes, as a function of pressure and temperature. We find that formation of a monolayer, and phase changes within a monolayer, affect the nanotube conductance. Isotherms of conductance as a function of pressure yield complementary information to coverage isotherms (obtained from the mass shift in the natural vibrational frequency of the nanotube). For example, we observe sharp features preceding first-order transitions in the monolayer. Also, the conductance changes can be measured on a timescale of milliseconds, permitting studies of the dynamics of the monolayer. In the nonlinear regime we observe features in the I-V characteristics as phase transitions are induced by the current, and stationary nonequilibrium states occur.

#### Influence of elastic strains on the adsorption process in porous materials

#### Annie Grosman and Camille Ortega

Institut des NanoSciences de Paris, Université Paris 6, UMR-CNRS 75-88

This work is the continuation of the investigation we are leading to explain the hysteretic behavior of fluid confined to porous materials taking into account the elastic deformation of the solids [1-5].

We study [6] the adsorption process of N<sub>2</sub> (77.4K and 51.3K) and Ar (60K) in porous silicon duplex layers, Si/A/B and Si/B/A, where the pores of A are narrower, on average, than the pores of B. We compare the experimental isotherms to that calculated from elemental isotherms measured in layers A and B supported by or detached from the silicon substrate.

In the ink-bottle Si/B/A configuration, layer B empties via cavitation. The liquid pressure at which cavitation occurs (e.g. -4.5MPa for  $N_2$  at 77.4K) is much higher than the value (-15MPa) predicted by the theory of homogeneous nucleation. Nucleation of gas bubbles takes place at the pore wall surface.

For a gas bubble at the surface of a pore wall, the contact angle between the solid and liquid is higher than  $\pi/2$  while, for a receding meniscus, it is lower than  $\pi/2$ . A receding meniscus inside a pore cannot coexist with a gas bubble at pore wall surface. This questions the pore-blocking models according to which cavitation originates from a meniscus blocked in a narrow section.

The number of pores is three times higher for layer A than for B so that, in the configuration Si/B/A, layer A has dangling pore walls at the interface between the two layers. The partial relaxation of the constraint modifies the adsorption strains which leads to a decrease of the adsorbed amount before condensation and consequently to an increase of the condensation pressure. These results confirm our previous studies which show the influence on the adsorption process of the elastic deformation of porous materials [4, 5].

For argon in the Si/B/A duplex layer, cavitation in layer B activates the emptying of a fraction of pores of layer A which constitutes a first direct observation of metastable states of the dense phase confined to mesopores.

<sup>[1]</sup> Coasne B., Grosman A., Ortega C. and Simon M. Phys. Rev. Lett. 88, 256102 (2002).

Gossnie B., Grösman A., Ortega C. Langmuir 21, 10515 (2005).
 Grösman A. and Ortega C. Langmuir 21, 10515 (2005).
 Grösman A. and Ortega C. Langmuir 24, 3877 (2008).
 Grösman A. and Ortega C. *Phys. Rev. B* 78, 055433 (2008).
 Grösman A. and Ortega C. *Langmuir* 25, 8083 (2009).
 Grösman A. and Ortega C. *Langmuir* 25, 8083 (2009).
 Grösman A. and Ortega C. *Langmuir* 27, 2364 (2011).

### Absorbent expansion/contraction driven by gas uptake: novel transitions for graphene and other substrates

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Increasing attention is being paid to the fact that absorbent materials react to the presence of adsorbed gas. The consequences can be dramatic in cases, like MOFs, for which the absorbent is particularly flexible or in other cases, like a nanotube bundle <sup>1,2</sup>, for which the adsorption potential is a very sensitive function of the adsorbent's geometry. This talk focuses on two very distinct examples. In one, an imbibition transition is predicted for the case of a graphene sheet lying on a silica, or other, supporting surface <sup>3</sup>. The other example is the case of when a small pore *elongates* in order to maximize the adsorbent area<sup>4</sup>.

Research supported by DOE

<sup>1</sup>M. Mercedes Calbi, Flavio Toigo and Milton W. Cole, Phys. Rev. Lett. 86, 5062-5065 (2001)

<sup>2</sup>F. Ancilotto, M. W. Cole, A. Grosman, E. S. Hernández and F. Toigo, Expansion or contraction of slit pores due to gas uptake, J. Low Temp. Phys. 163, 284-301 (2011)

<sup>3</sup>Kate E. Noa, Angela D. Lueking and Milton W. Cole, Imbibition transition: gas intercalation between graphene and a solid surface, J. Low Temp. Phys.163, 26-33 (2011)

<sup>4</sup>M. W. Cole and A. Grosman, Significant elongation of a pore due to adsorption, unpublished

### Stability requirements for square monolayer lattices in physical adsorption

#### L. W. Bruch

Department of Physics, University of Wisconsin-Madison

Properties of square commensurate monolayer lattices and structures that compete with them in stability are discussed. The features addressed are: (1) the conditions that the commensurate lattice is formed at monolayer condensation, (2) what the requirements are that the structure that succeeds the commensurate square under compression is a commensurate square bilayer lattice; and (3) signatures in the lattice dynamics of the commensurate square monolayer. Examples from physical adsorption are Kr/NaCl(001),  $H_2$ /NaCl(001), and CH<sub>4</sub>/MgO(001). The Kr/NaCl(001) case has been published<sup>1</sup> and the CH<sub>4</sub>/MgO(001) case is part of ongoing work.<sup>2</sup>

<sup>1</sup>L. W. Bruch, J. Phys. Chem. A **115**, 6882 2011). <sup>2</sup>L. W. Bruch and J. Z. Larese, (to be published).

### Helium 4 in Nanoporous Media: Effect of Confinement and Disorder

#### Keiya Shirahama

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Liquid and solid <sup>4</sup>He are a strongly correlated Bose system, in the sense that quantum properties are suppressed by interatomic correlation. By confining <sup>4</sup>He to nano-porous media, one can control the interplay between quantum and correlation effects. Porous media can also introduce disorder and topological structures to originally clean (impurity-free) and isotropic <sup>4</sup>He. As a result novel ground states other than superfluid and crystalline states can be realized; e.g. Bose glass, Mott insulator, and supersolid.

In this talk I will discuss the effects of confinement and disorder on superfluidity of <sup>4</sup>He in nanoporous glasses: (1) Torsional oscillator and heat capacity studies have revealed an interesting quantum phase transition (superfluid – "insulator" transition) at pressures around 3 MPa. This novel behavior is related to the emergence of localized BEC states, in which the macroscopic phase coherence is destroyed by the strong confinement<sup>[1]</sup>. (2) The superfluid transition of thin <sup>4</sup>He films adsorbed in a porous glass is suppressed by preplating a monolayer of krypton. The suppression of film superfluidity is attributed to the quantum localization of <sup>4</sup>He atoms by the randomness in the substrate potential, which is caused by the preplating-induced broadening of the pore size distribution<sup>[2]</sup>.

<sup>[1]</sup> K. Yamamoto et al. Phys. Rev. Lett. 100, 195301 (2008).

<sup>[2]</sup> Y. Shibayama and K. Shirahama, J. Phys. Soc. Jpn. 80, 084604 (2011).

#### 3D and 1D Superfluids of <sup>4</sup>He Films Formed in Nanopores

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Department of Physics, Nagoya University, Chikusa-ku, Nagoya, Japan

We have studied superfluid densities and heat capacities of <sup>4</sup>He films adsorbed in two kinds of nanoporous powders, organic-inorganic hybrid HMM-2 and folded silicate FSM. They have very similar adsorption potential for <sup>4</sup>He and show similar <sup>4</sup>He film growth, but have quite different pore structures which are expected to manipulate the superfluid dimensionality.

In 3D pore network of HMM-2 where 2.7 nm pores are regularly connected with the 3D period 5.5 nm, the heat capacity of <sup>4</sup>He film has a small but sharp peak at the superfluid onset temperature observed by a torsional oscillator. It is characteristic of a 3D superfluid transition, clearly distinguished from Kosterlitz-Thouless (KT) transition of flat 2D film with no heat capacity anomalies. As temperature lowers, the heat capacity peak becomes sharper and larger, which can be explained by that the peak representing the 3D transition appears when the correlation length becomes longer than the 3D period of pores. Interestingly, the temperature dependence of superfluid densities and the coverage dependence of superfluid onset temperatures are observed similarly to those of atomic 3D Bose gas.

For straight 1D nanochannels in FSM about 300 nm, superfluid <sup>4</sup>He has been observed in channels larger than 1.8 nm, even in 1D phonon states with *T*-linear heat capacities. Especially in 2.4 nm channels, the superfluid density in channels is definitely observed to grow gradually towards lower temperatures, of which characteristic temperature is indicated by a large broad dissipation peak at lower temperatures than the KT transition of 2D film. According to recent theoretical studies, superfluidity in the 1D system is suppressed by  $2\pi$  phase windings excited via the phase slippage, instead of long-wave phonons or free vortices in 2D film. Though the characteristic temperature determined by the 1D <sup>4</sup>He density and system length is zero in infinitely long 1D system, that for 300 nm becomes even comparable to the KT temperature, depending on the channel size. Considering also the dynamic effect of phase winding excitations, the observed increases of superfluid densities are consistent with the expected for the finite-length 1D superfluid.

### Towards DFT calculations of metal clusters in quantum fluid matrices

#### E. Krotscheck and M. Liebrecht

Institute for Theoretical Physics, JKU Linz, Austria; Department of Physics, University at Buffalo SUNY

This paper reports progress on the simulation of metallic clusters embedded in a quantum fluid matrix such as He-4. A key issue is that the interaction between a helium adatom and a metal cluster can be very different from the interaction between isolated atoms; this is due to the potential (de-)localization of electrons in the cluster. Examples of the electron density in Mg\_n and Na\_n clusters document the effect.

We report here a semi-phenomenological approach for determining the clusteradatom interactions. The long ranged part determined by both the static and the induced electric fields in the cluster. The induced polarization of the valence electrons recovers the long-ranged part of the interaction; the short-ranged portions are obtained from quantum chemistry calculations. The comparison of potentials obtained from a simple (conducting) jellium model for an Mg cluster with a DFT calculation that predicts localized electron orbitals documents the effect of electron delocalization.

We also show how a naïve implementation of density functional theory fails to recover the correct physics.

# Recent advances on the adsorption of superfluid helium in nanostructured surfaces and nanopores: a density functional approach

#### Susan Hernández

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina

In this talk I review some highlights of the last decade regarding structure and energetics of finite samples of helium adsorbed in substrates of various geometries at very low temperatures. I discuss the evolution of edge states populated by a single 3He atom at the contact line of a 4He droplet deposited on a weak adsorber. I illustrate the appearance of hysteresis and symmetry breaking along adsorption paths. The thick film-thin film coexistence on flat surfaces is revisited aiming at the possibility of computing line and border tensions in the different regions of the thermodynamic phase space for adsorption of helium.

# Adsorption isotherms on individual suspended single-walled carbon nanotubes using vibrational resonance frequency measurements<sup>\*</sup>

Oscar E. Vilches, Zenghui Wang, Richard Roy, Hao-Chun Lee, Erik Fredrickson and David H. Cobden

Department of Physics, University of Washington, Seattle, WA

In this presentation we will describe measurements of the mass adsorption of <sup>4</sup>He, Ar and Kr on a vibrating suspended, single-walled carbon nanotube with sensitivity of a few atoms<sup>1</sup>. In essence, the resonance frequency of a nanotube grown across a trench with Pt electrodes on each side in a silicon wafer is measured as a function of a regulated constant temperature and quasi-equilibrium pressure inside the vacuum enclosure. Much like for the strings of a guitar, the square of the resonance frequency is proportional to the inverse of the mass of the nanotube plus adsorbate. The resonance frequencies are in the 10 to 500 MHz range. For <sup>4</sup>He we measured three isotherms between 4.4 and 6.4 K on one device. For Ar and Kr we measured multiple isotherms on several devices over a wide temperature range. We can outline phase diagrams for Ar and Kr, and calculate the isosteric heat of adsorption for the three gases, which are all smaller than for adsorption on graphite. Successes and difficulties will be discussed.

<sup>\*</sup> Work supported by NSF DMR 0907690

1. Z. Wang, J. Wei, P. Morse, J. G. Dash, O. E. Vilches and D. H. Cobden, Science 327, 554 (2010).

### **Adsorption Kinetics of Polyatomic Molecules**

#### Jared T. Burde and M. Mercedes Calbi

Department of Physics and Astronomy, University of Denver, Denver, CO

Adsorption equilibration times for polyatomic molecules on nanotube bundles have been observed to increase with final amount adsorbed. This is in contrast to what happens for simpler mono-atomic adsorbates that show a decrease in equilibration time with coverage. By examining the role of adsorbate-adsorbate interactions as well as the energy heteregoneity of the system (given by either the polyatomic nature of the adsorbate or the heterogeneity of the surface, or both), we are able to identify the conditions responsible for each one of the observed kinetic behaviors.

### Studies of the layering in alkane films adsorbed on a solid surface

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Two systems have been studied experimentally by neutron diffraction, guasielastic neutron scattering, and by molecular dynamics simulations: A onecomponent system of an intermediate-length alkane, triacontane  $(n-C_{24}H_{50})$ ; and a binary mixture of a short alkane, heptane  $(n-C_7H_{16})$ , and a longer alkane, dotriacontane ( $n-C_{32}H_{66}$ ). In the binary system, we have studied the selective adsorption of the long alkane, interlayer transitions of molecules in the heptane layers above a monolayer of dotriacontane molecules, and diffusive motion within the different heptane layers at temperatures above the bulk melting point of heptane and below the melting point of the dotriacontane monolayer. The diffusion constants for molecules in the different layers depend strongly on the molecular density in the layers and only moderately on the molecules in the neighboring layers. In the one-component system of triacontane molecules, we have also studied interlayer transitions and diffusive motion within the different layers at temperatures around the melting temperature of the triacontane monolayer. We show that the addition of molecular layers above the monolayer stabilizes the film and results in an increase in the melting point of 10-15 % above that of the monolayer.

### Adsorption at the Nanoscale - Posters

(in alphabetical order by presenter's last name)

Poster	Poster Title	Presenter		Affiliation
17	Adsorption of CO2 on open single walled carbon nanohorn aggregates	Shree	Banjara	Southern Illinois University
2	Analysis of hydrogen sorption characteristics of boron-doped activated carbons	Matthew	Beckner	University of Missouri
16	The Adsorption of Interacting Particles on a Carbon Nanotube Bundle	Jared	Burde	University of Denver
1	Gas Sorption Studies of Graphene Oxide Frameworks	Jacob	Burress	NIST Center for Neutron Research
15	Design of Advanced Sorbent Materials with Enhanced Sorption Capability and Chemical Reactivity	Pabitra	Choudhury	University of Pittsburgh
23	Flexible Pore Walls in Activated Carbon	Matthew	Connolly	University of Missouri
6	The reversibility of the adsorption of methane-methyl mercaptan mixtures in nanoporous carbon	Monika	Golebiowska	University of Missouri
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### Adsorption of CO<sub>2</sub> on Open Single Walled Carbon Nanohorn Aggregates

<u>Shree Banjara<sup>a</sup></u>, Vaiva Krungleviciute<sup>a</sup>, Aldo D Migone<sup>a</sup>, Masako Yudasaka<sup>b</sup>, Sumio Iijima<sup>c</sup>

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Single-walled dahlia-like carbon nanohorns treated with  $H_2O_2$  for 3 hrs at 150  $^{0}$ C were used as sorbent in a study of CO<sub>2</sub> adsorption. This treatment ensures that the nanohorns are open and they have their interior space available for adsorption. Volumetric adsorption measurements on open spherical aggregates of dahlia-like single walled carbon nanohorns were performed at seven different temperatures between 162 and 212 K. The waiting time for reaching the equilibrium pressure after adding a dose increased with sorbent loading. Unlike Ne and CF<sub>4</sub> adsorption isotherms measured on similar substrate which have two distinct substeps present in the isotherms, the adsorption data for CO<sub>2</sub> has a single very broad step present between the lowest coverage and saturation. Results for the loading dependence of the isosteric heat and an estimate for the low coverage binding energy are being investigated and will be presented. Results for the effective specific surface area of the open single walled carbon nanohorns sample obtained in this study will be compared with the ones obtained with other carbon nanohorn samples.

### Analysis of hydrogen sorption characteristics of boron-doped activated carbons

<u>Matthew Beckner</u><sup>1,2</sup>, Matthew Connolly<sup>1,2</sup>, Jimmy Romanos<sup>1,2</sup>, David Stalla<sup>1,2</sup>, Elmar Dohnke<sup>1,2</sup>, Anupam Singh<sup>1,3</sup>, Mark Lee<sup>1,3</sup>, Satish Jalisatgi<sup>1,3</sup>, Galen Suppes<sup>1,4</sup>, M Frederick Hawthorne<sup>1,3</sup>, Ping Yu<sup>1,2</sup>, Carlos Wexler<sup>1,2</sup>, Peter Pfeifer<sup>1,2</sup>

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<sup>4</sup>University of Missouri, Department of Chemical Engineering, Columbia, MO USA

There is significant interest in the properties of boron-doped activated carbons for their potential to improve hydrogen storage.<sup>1</sup> Boron-doped activated carbons have been produced using a novel process involving the pyrolysis of a boron containing compound and subsequent high-temperature annealing. In this poster we will present a systematic study of the effect of different boron doping processes on the samples' surface area, micropore structure, and hydrogen sorption. Experimental results include boron content from prompt gamma neutron activation analysis, boron-carbon chemistry from Fourier transform infrared spectroscopy (FTIR), nitrogen subcritical adsorption, and 80K and 90K hydrogen adsorption isotherms which allow us to evaluate the hydrogen binding energy for each sorptive material. Additionally, a theoretical study of the interaction of the boron containing compound with the undoped carbon precursor will be presented. The theoretical study outlines the unique capabilities and limits of this doping procedure.

#### <sup>1</sup>See http://all-craft.missouri.edu

<sup>2</sup>This material is based on work supported by the US Department of Defense under Awards No. N00164-07-P-1306 and N00164-08-C-GS37 and the US Department of Energy under Awards No. DE-FG02-07ER46411 and DE-FG36-08GO18142.

### The Adsorption of Interacting Particles on a Carbon Nanotube Bundle

Jared T. Burde, M. Mercedes Calbi

University of Denver

Carbon nanotubes hold great promise for adsorption applications. A bundle of carbon nanotubes has a high surface area density and can have a narrow poresize distribution. However, the process by which particles adsorb in carbon nanotube bundles is still not well understood. In particular, it is not clear how fast the adsorption process is, an important consideration when deciding how long to allow a system to equilibrate before taking an isotherm measurement. Our work endeavors to fill this knowledge gap by simulating the adsorption of particles on carbon nanotube bundles and measuring the waiting time required for the system to reach equilibrium.

We have implemented a Kinetic Monte Carlo scheme to simulate the adsorption of molecules on a carbon nanotube bundle. This algorithm allows us to track the number of molecules adsorbed to the surface as a function of time, allowing us to measure the coverage as a function of time, from which we can extract the equilibration time of the system.

In this work we have focused on the effect of particle-particle interactions on the kinetic behavior of the system. We have run simulations to look at how the strength of particle-particle interactions affects the equilibrium state and the equilibration time. We have also employed a two-dimensional, heterogeneous lattice to better model the reality of the exterior surface of a carbon nanotube bundle. The results we have produced have given us insight into the parameters that have the greatest effect on the adsorption process.

#### Gas Sorption Studies of Graphene Oxide Frameworks

Jacob Burress, Gadipelli Srinivas, Wei Zhou, Taner Yildirim NIST Center for Neutron Research, Gaithersburg, MD USA

By using the well-known chemistry between boronic acids and hydroxyl groups, graphene oxide layers can be linked together to form a new layered structure, graphene oxide frameworks. The GOF structures develop through boronate-ester formation as a result of B-O bonding between boronic acids and oxygen functional groups on the GO layers. Synthesized GOFs exhibit periodic layered structures with largely expanded interlayer spacing as characterized by X-ray powder diffraction (XRD). The boronate-ester link formation is further evidenced by Fourier transform infrared (FTIR) and Raman spectroscopy. Furthermore, the strong boronate-ester bonds between GO layers results in improved thermal stability over the precursor GO. Despite low surface area, GOFs exhibit 1 wt% H2 uptake at 1 bar. This is much less than what the ideal GOF structure can hold, suggesting that our initial GOF materials could be significantly optimized. Initial GOF materials exhibit isosteric heats at zero coverage of 9 kJ/mol and 32 kJ/mol for H2 and CO2, respectively; comparable to metal-organic frameworks (MOFs) with open metal centers. This enhanced Qst and adsorption capacity is attributed to optimum interlayer spacing between graphene planes such that hydrogen molecules interact with both surfaces. The solvent-free, evacuated frameworks provide highly increased accessible surface area for nitrogen adsorption compared to GO alone, which depends on the type and length of the boronic acid, indicating the importance of pillaring unit. Finally, our systematic study reveals the profound effect of both synthesis and activation temperatures to obtain porous framework structures. Powder x-ray diffraction revealed tunable interlayer spacing, reaching a maximum once the interlayer space has been saturated by linkers. Results on the hydrogen dynamics from neutron spectroscopy of these systems will be presented. In the future, GOF structures will be synthesized with tunable pore widths, volumes, and binding sites depending on the linkers chosen.

#### Design of Advanced Sorbent Materials with Enhanced Sorption Capability and Chemical Reactivity

<u>Pabitra Choudhury<sup>a</sup></u>, J. Karl Johnson<sup>a</sup>, Lynn Mandeltort<sup>b</sup>, Michael Büttner<sup>b</sup>, and John T. Yates, Jr.<sup>b</sup>

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Carbon materials, specially, single walled carbon nanotubes (SWNTs) and highly ordered pyrolytic graphite (HOPG), have been shown to readily and reversibly adsorb many gases through van der Waals (vdW) forces. However, pure SWNTs and HOPG are not considered useful in cases where very strong or irreversible adsorption is required, such as in capture of toxic gases. Importantly, adsorption energies can be substantially enhanced and chemical reactions can be facilitated through doping and functionalization of these carbon materials. We present combined experimental and theoretical results that show how alkali metal doped SWNTs and HOPG can act as chemically reactive sorbents that irreversibly break carbon-chlorine bonds in chloroalkanes. Furthermore, we show that the alkyl groups liberated from the C—CI bond scission can be bound to defect sites and edge sites on the carbons. Our density functional theory (DFT) calculations reveal that the C—CI bond scission proceeds by a two-step reaction pathway and that at least two Li atoms are needed to break this bond at appreciable rates at the low temperatures of the experiments; one Li atom is consumed to form LiCl, while the second Li atom acts as a catalyst to lower the energy of the first step of the reaction. This finding could prove useful for capturing and detoxification of toxic chemicals with other key functional groups (e.g. -C=N, C-S-C, -P=O) on high area advanced carbon sorbents.

### Flexible Pore Walls in Activated Carbon

#### Matthew J. Connolly and Carlos Wexler

University of Missouri, Department of Physics and Astronomy, Columbia, MO

Adsorbent materials such as activated carbon and Metal-Organic Frameworks (MOFs) have received significant attention as a potential storage material for hydrogen and natural gas. Typically the adsorbent material is assumed to consist of rigid slit- or cylindrical-shaped pores. Recent work, for MOFs in particular, revealed the importance of the mechanical response of the adsorbent in the presence of an adsorbate. Here, we demonstrate the flexibility of pore walls in activated carbon and the effect this has on the pore structure of the bulk samples. The interaction is modeled as a competition between Van der Waals interactions between neighboring walls and a resistance to bending due to the rigidity of graphene. Minimal energy configurations were calculated analytically for a simplified potential and numerically for a more realistic potential. The pore structures are discussed in the context of pore measurements on activated carbon samples.

### The reversibility of the adsorption of methane–methyl mercaptan mixtures in nanoporous carbon

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Methane is a main constituent of natural gas (NG). As a fuel for vehicular applications NG requires sorbents that allow efficient, reversible, safe storage at room temperature and moderate pressure. To provide an easy human detection of the gas leak from the adsorbed natural gas (ANG) system, we propose that the gas could be added with compounds having low odor threshold, such as thiols (mercaptans). The results of extensive molecular dynamics simulations and theoretical considerations of the adsorption of methane-methyl mercaptan mixtures in slit-shaped carbon nanopores are presented. We observe significant mobility of both methane and mercaptan molecules within the pore volume, between pores, and between adsorbed and gas phases for a wide range of temperatures and pressures. Although mercaptans adsorb preferentially relative to methane, the process remains reversible, provided non-oxidizing conditions are maintained. A mercaptan/methane ratio of the order of 200 ppm in the adsorbed phase is sufficient for the gas phase to have a mercaptan concentration above the human threshold for detection. The reversibility of the adsorption process and low concentration of mercaptans makes it unlikely that these would be harmful for adsorbed natural gas storage systems.

This work was supported in part by the California Energy Commission under Contract No. 500-08-022.

#### **Cryogenic Storage of Methane on Activated Carbon**

A. Tekeei, <u>R. Hilton</u>, P.A. Bick, S.A. Absher, and L. Guo Department of Chemical Engineering, University of Missouri, Columbia, MO

As a means to improve the capacity of activated carbon for storage of natural gas, adsorption isotherms were measured on ALLCRAFT carbon at temperatures of -25, 0, and 25 C. The results indicated that lower temperatures improve storage capacity; however, increases at moderate pressures (200-500 psia) are not has great as would be desired. Studies continue to identify those factors that limit and improve the ability of cryogenic temperatures to improve the adsorption capacity of natural gas.

### The Internal Degrees of Freedom of Layered Graphene Structures: a Molecular Dynamics

C. Hubbard, M. Kaspar, T.E. Kidd and M.W. Roth

Physics Department, University of Northern Iowa, Cedar Falls, IA USA

We present the results of Molecular Dynamics computer simulations of graphene nanostructures subject to the constraints of differing boundary conditions. The systems have both odd and even numbers of graphene sheets with various spacings; NAMD simulation with a CHARMM force field are utilized. Emphasis is placed on studying the static and dynamic behavior of the three internal degrees of freedom - bond stretching, bond angle bending and dihedral torsion.

#### Sensing Phase Behavior of Noble Gases on Individual Single-Walled Carbon Nanotubes

<u>H.C. Lee</u>, B. Dzyubenko, E. Fredrickson, R. Roy, Z. Wang, O.E. Vilches, D.H. Cobden

Department of Physics, University of Washington, Seattle WA

Suspended single-walled carbon nanotubes can act simultaneously as onedimensional transistors and nanomechanical resonators which have the ability to detect the adsorbed substance with very high sensitivity. We have studied the adsorption of a series of noble gases, from He to Xe, on nanotubes under conditions of controlled pressure and temperature. From the change in resonant frequency due to mass loading we obtain isotherms of coverage, which exhibit behavior similar to that on graphite but with notable differences, including weaker binding energies. We have also investigated how the conductance changes in the presence of vapor, obtaining conductance isotherms which yield complementary information to the coverage. Even formation of a monolayer of helium can have a large effect on the conductance, as a result of charging effects. The conductance can be measured with a high bandwidth, allowing investigations of the dynamics of adsorption. Also, we observe negative differential resistance features in the I-V characteristics as phase transitions are induced by the current. At these features we sometimes see metastable states, asymmetric in bias, which are indicative of stationary nonequilibrium states. These appear to have some relationship to sharp, unexplained features observed adjacent to first-order phase transitions in the conductance isotherms.

#### Design and Construction of Bio-MOFs for CO<sub>2</sub> and H<sub>2</sub> Adsorption

Tao Li, Mark Kozlowski, Jihyun An, Nathaniel L. Rosi

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA

We have initiated a research program aimed at using simple biomolecules as building blocks for porous metal-organic crystalline materials. We are targeting such materials because of their potential biological and environmental compatibility, aspects that are important for environmental applications environmental clean-up/remediation), biomedical (e.g. applications (e.g. NO delivery, drug delivery, enzyme sequestration) as well as gas adsorption and separation (e.g.  $CO_2/N_2$  separation,  $H_2/CH_4$  storage). In this work, we explore the coordination chemistry between metal ions and adenine in the context of constructing discrete and extended coordination assemblies. We also examine and tune their adsorption properties via various methods to understand potential factors that can affect their sorption behavior.

### Controlling the Kinetics and Decomposition Pathway of LiBH<sub>4</sub> via Confinement in Highly Ordered Nanoporous Carbon

Xiangfeng Liu, David Peaslee, Christopher Z. Jost, and Eric H. Majzoub

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In addition to conventional strategies for improving kinetics and thermodynamics of metal hydrides, including the use of catalyst dopants or destabilization, the effect of nanoscale size, through confinement in templates or frameworks, has attracted increasing attention. The decomposition thermodynamics and kinetics of LiBH<sub>4</sub> has been investigated in the presence of highly ordered nanoporous carbon (NPC) with a 2D-hexagonal geometry, a narrow size distribution, and different pore sizes. LiBH<sub>4</sub> confined within 2 nm highly-ordered columnar pores becomes amorphous. The nano-confinement results in the disappearance of the structural phase transition and the melting transition, a significant decrease of the onset desorption temperature, and suppresses diborane release. The reaction pathway is likely altered through a strong interaction with the carbon template. We illustrate the wetting behavior of LiBH<sub>4</sub> on infiltration NPC using differential scanning calorimetry, and discuss the implications of the wetting behavior on the decomposition pathways. The systematic pore-size effects of nanoconfinement of LiBH<sub>4</sub> will also be presented.

### Study of water diffusion on single-supported bilayer lipid membranes by quasielastic neutron scattering\*

<u>A. Miskowiec</u><sup>1</sup>, M. Bai<sup>1</sup>, F. Y. Hansen<sup>1</sup>, H. Taub<sup>1</sup>, T. Jenkins<sup>2</sup>, M. Tyagi<sup>2,3</sup>, D. A. Neumann<sup>2</sup>, S. O. Diallo<sup>4</sup>, E. Mamontov<sup>4</sup>, K. W. Herwig<sup>4</sup>, and S.-K. Wang<sup>1</sup>

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Bilayer lipid membranes supported on a solid surface are attractive model systems for understanding the structure and dynamics of more complex biological membranes that form the outer boundary of living cells. We have recently obtained high-energy-resolution quasielastic neutron spectra from single-supported bilayer lipid membranes using the backscattering spectrometers at the NIST Center for Neutron Research and the Spallation Neutron Source at Oak Ridge National Laboratory. DMPC membranes were deposited onto SiO<sub>2</sub>coated Si(100) substrates and characterized by AFM. Analysis of their neutron spectra shows evidence of a relatively broad Lorentzian component that we identify with bulk-like water above a freezing temperature of ~267 K. At lower temperatures, the spectra differ qualitatively from that of bulk supercooled water, a behavior that we attribute to water confined to a region near the lipid head groups. We also find evidence of a narrow Lorentzian component that we tentatively identify with a slower motion (time scale ~1 ns) associated with the center-of-mass motion of the lipid molecules and water bound to their head groups. A second sample with about 10 times lower level of hydration and deuterated lipid tails was also investigated. From the intensity ratio of the narrow Lorentzian component in the two samples, we infer about 9  $H_2O$  molecules bound per lipid head group in reasonable agreement with NMR experiments on multilamellar DMPC samples.

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### Spectroscopic Evidence for H<sub>2</sub>-H<sub>2</sub> interactions in Metal Organic Frameworks (MOFs) with unsaturated metal centers

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Metal Organic frameworks are being considered for hydrogen storage because of their excellent hydrogen adsorption and release rates, their tailorable structures and high surface area. Unlike materials that chemically incorporate hydrogen via dissociation and chemical bonding, and require heating for H<sub>2</sub> release, MOFs utilize physisorption as the adsorption mechanism. They are crystalline so that hydrogen adsorbs at specific adsorption sites.

This work explores  $H_2$ - $H_2$  interactions between adsorbed  $H_2$  in different binding sites in MOF-74 (M<sub>2</sub>(dhtp),dhtp=2,5-dihydroxyterephthalate) that is composed of unsaturated metal centers. Combining vdW-DFT calculations and IR spectroscopic techniques we are able to characterize these interactions by monitoring the IR shifts (from the unperturbed H<sub>2</sub> stretch frequency) and the dipole moments of adsorbed H<sub>2</sub>. In MOF-74, these adsorption sites are, in order of decreasing binding energy, the metal, oxygen, benzene and center sites, as determined by neutron scattering by Liu et al. Our study shows that the IR shifts and dipole moment of adsorbed  $H_2$  are greatly affected by  $H_2$ - $H_2$  interactions. The frequency of adsorbed  $\rm H_2$  at the metal site suffers an additional  $\sim\!\!-30~\rm cm^{-1}$  red shift (for Mg and Zn) and ~-84 cm<sup>-1</sup> (for Co) when the neighboring oxygen site is occupied due to H<sub>2</sub>-H<sub>2</sub> interaction of a "pair" of hydrogen atoms. The dipole moment of adsorbed H<sub>2</sub> at the metal site also decreases when the oxygen site is occupied. The larger shift observed for the cobalt case can be attributed to the proximity of the H<sub>2</sub> molecules to the structure. IR measurements performed at 77 K show the appearance of the IR band corresponding to such a pair (i.e. occupation of both the metal and oxygen sites) even at low loading (when all metal sites are not occupied).

### Direct Line-of-site Gas Desorption Study of LiBH<sub>4</sub> in Nanoporous Carbons: The Influence of Surface Chemistry and the Size Effect

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Thermodynamic and kinetic properties of metal hydrides may differ between bulk and nano-sized particles. By adjusting the size of these particles through confinement in nano-porous materials, properties including the hydrogen sorption rate and possibly temperature can be fine-tuned to meet engineering requirements for real-world systems. Studies of nano-structured carbon materials infiltrated with LiBH<sub>4</sub> reveal differences in the decomposition pathway that depend on the carbon nano-pore size and the surface chemistry. We present results of gas desorption using a direct line-of-site residual gas analyzer mass spectrometer (RGAMS) system to characterize gas desorption species, and decomposition temperatures, and differences in reaction pathways, for a variety of LiBH<sub>4</sub>/carbon systems. The RGAMS is a differentially-pumped, two-chamber line-of-sight measurement device with a sensitivity of ~1x10<sup>-10</sup> Torr of partial pressure. We present results for 9-14 nm carbon aerogels and 2-4 nm highly ordered nano-porous carbons consisting of columnar pores packed in a hexagonal geometry. RGAMS results, together with XRD, FTIR, and calorimetry studies, indicate that pore size, non-crystallinity of the LiBH<sub>4</sub>, and surface chemistry all play a role in formation of diborane  $(B_2H_6)$  during the infiltration process and also during desorption of melt-infiltrated materials. While all materials show diborane formation during melting under vacuum, not all previously melt-infiltrated carbons show diborane formation during decomposition. We discuss the materials and possible causes for the formation of diborane in some carbons.

### The effect of KOH:C and activation temperature on hydrogen storage capacities of activated carbons

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The Alliance for Collaborative Research in Alternative Fuel Technologies (ALL-CRAFT<sup>1</sup>) has been producing high surface area activated carbons. Here we will investigate the effect of the ratio of activating agent to carbon and activation temperature on hydrogen sorption characteristics and sample structure. Results show that a ratio of 3:1 KOH:C and an activation temperature of 790 C are the ideal activation conditions for hydrogen storage applications. Hydrogen sorption measurements are completed using a volumetric instrument that operates at pressures up to 100 bar and at temperatures of 80 K, the sublimation temperature of dry ice (-78.5 C), and room temperature. Specific surface area and pore size distributions are measured using subcritical nitrogen isotherms.

<sup>1</sup>See <u>http://all-craft.missouri.edu</u>

<sup>2</sup>This material is based on work supported by the US Department of Defense under Awards No. N00164-07-P-1306 and N00164-08-C-GS37, the US Department of Energy under Awards No. DE-FG02-07ER46411 and DE-FG36-08GO18142.

#### Natural Gas Storage in Nano-porous Activated Carbon

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Adsorbed natural gas (ANG) technology is an energy efficient method for storing natural gas at room temperature and low pressure. The Alliance for Collaborative Research in Alternative Fuel Technology (ALL-CRAFT http://all-<u>craft.missouri.edu/</u>) has developed activated carbons from corn cobs as adsorbent materials for natural gas storage by physisorption at low pressures. Activated carbons were optimized for storage by varying KOH to carbon weight ratio and activation temperature. Mapping the pore structure at the nanometer scale is fundamental for the understanding of adsorptive properties. Small-angle x-ray scattering (SAXS), subcritical nitrogen adsorption isotherms and transmission electron microscopy (TEM) were used to characterize the porous structure of amorphous activated carbons. Record Methane gravimetric and volumetric storage capacities of 250 g CH<sub>4</sub>/kg carbon and 132 g CH<sub>4</sub>/liter carbon at 35 bar and 293 K have been achieved.

This material is based on work supported by the California Energy Commission under Contract No 500-08-022. Use of the Advanced Photon Source was supported by the U.S. Department of Energy under Contract No. DE-AC02-06CH11357.

### Boron-neutron Capture on Activated Carbon for Hydrogen Storage

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This work presents the effects of neutron irradiation of boron-doped activated carbon on nitrogen and hydrogen adsorption. Boron-neutron capture generates energetic lithium nuclei, helium nuclei, and gamma photons that bore through the carbon matrix upon fission. In order to explain the effect of irradiation on the surface area, the defects introduced by fission tracks are modeled on a homogeneous slit shaped pore matrix. This process alters the surface and the pore structure of activated carbon. Sub-critical nitrogen adsorption shows that nitrogen molecules are inadequate to probe the defects introduced by fission tracks. Surface area and binding energies were determined from supercritical hydrogen adsorption. Hydrogen adsorption isotherms of irradiated samples are indicative of higher binding energies and a larger fraction of sub-nanometer pores compared to their non-irradiated parent samples.

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#### A high volume, high throughput volumetric sorption analyzer

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In this talk we will present an overview of our new Hydrogen Test Fixture (HTF) constructed by the Midwest Research Institute<sup>1</sup> for The Alliance for Collaborative Research in Alternative Fuel Technology<sup>2</sup> to test activated carbon monoliths for hydrogen gas storage. The HTF is an automated, computer-controlled volumetric instrument for rapid screening and manipulation of monoliths under an inert atmosphere (to exclude degradation of carbon from exposure to oxygen). The HTF allows us to measure large quantity (up to 500 g) of sample in a 0.5 I test tank, making our results less sensitive to sample inhomogeneity. The HTF can measure isotherms at pressures ranging from 1 to 300 bar at room temperature. For comparison, other volumetric instruments such as Hiden Isochema's HTP-1 Volumetric Analyser can only measure carbon samples up to 150 mg at pressures up to 200 bar.

<sup>1</sup>http://www.mriresearch.org <sup>2</sup>http://all-craft.missouri.edu

<sup>3</sup>Work supported by the US DOD Contract # N00164-08-C-GS37.

### Nanopore structure from small angle and ultra-small angle x-ray scattering in engineered activated carbons for hydrogen storage

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High-surface-area activated carbons are an extraordinarily promising material for hydrogen storage<sup>†</sup>. However, despite their mass-production and industrial use, there is still no generally accepted structural model of non-graphitizing activated carbons. Mapping the pore structure at the nanometer scale is fundamental for the understanding of adsorptive properties. We will show how USAXS/SAXS can be used to estimate the average shape and size of nanopores in amorphous carbon used for hydrogen storage. Synthetic scattering curves constructed from explicit experimental nitrogen isotherm pore size distributions reveal that nanoporous activated carbons scatter as correlated networks of pores with scattered intensities that depend largely on sample porosity, the pore volume per sample volume. Graphical methods will be used to show how porosity can be calculated from SAXS data, using minimal model-dependent assumptions. The results are shown to be in excellent agreement with porosity values measured via subcritical nitrogen absorption isotherms. Additionally, this method allows calculation of the pore wall widths, which is not obtainable from traditional nitrogen isotherms. The data gathered from x-ray scattering will be compared to hydrogen adsorption and storage performance.

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#### A Molecular Dynamics Study of the Low - Temperature Rotational Transition in Fullerenes Adsorbed Onto Graphite

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All – atom molecular dynamics (MD) computer simulations of fullerene patches adsorbed onto graphite are conducted at various coverages for very low temperatures. There appears to be a continuous hindered low - temperature rotational transition seen in the simulations that accompanies dramatic lattice expansion and configurational energy change with temperature in the adlayer. We present and discuss results for the C60 system and extend them to study how the sharpness of the rotational transition depends on molecular smoothness vis - a- vis the difference between it static and dynamic shapes.

### Pore Structure Optimization for Methane Storage in Carbon Nanospaces

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The Alliance for Collaborate Research in Alternative Fuel Technology (ALL-CRAFT) has been researching hydrogen and methane gas storage via activated carbon as alternative options to the typical gasoline powered internal combustion engine vehicle. We have used methane gravimetry in an attempt to optimize the volumetric storage capacity of methane in carbon nanospaces. Although many of the samples have not yet achieved the desired outcome, it is noteworthy to point out that some samples are yielding very promising results, outperforming the rest at a level not commonly seen before. Gravimetric storage data as well as structural characteristics obtained from subcritical nitrogen isotherms will be presented for several samples produced in a parametric study investigating the effect of KOH:C and activation temperature during sample fabrication. As of mid July, 2011, the lab has made tentative alterations to the previously established procedure in order to optimize the volumetric storage density of activated carbon, achieving 132 g/l and surpassing the ANG Department of Energy target of 118 g/l. Continued research in this area therefore seems hopeful.

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### Kinetic Monte Carlo Study of TPD Spectra: Effects of Surface Heterogeneity

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We investigate gas desorption from external surfaces of carbon nanotube bundles by using a Kinetic Monte Carlo scheme. We explore desorption of quasispherical molecules that arrange themselves in three or five lines during adsorption, depending on molecule size. By varying the initial coverage and keeping track of the particles as they desorb and diffuse across the lines, we observe the effects of surface heterogeneity on Temperature Programmed Desorption (TPD) spectra. We perform these simulations for non-interacting, as well as interacting particles, and we compare our results to available experimental results.

#### Quasi-2D superfluid helium in solid helium in aerogel

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Two sharp phonon-roton curves provide evidence for the presence of superfluid helium within solid helium confined into aerogel at high pressures up to 54bar and low temperatures down to 50mK. The roton-gap parameters of these modes are clearly distinct from those of the bulk rotons. Mcroscopic many body calculations lead to the conclusion that the excitations correspond to rotons propagating in liquid double layers within the solid helium and at the solid helium substrate interface. Annealing at 1.3K leads to crystallization of the superfluid double layers inside the solid helium, whereas the roton excitation corresponding to a mode that lives at the liquid-solid interface stays unaffected. The crystallization process is revealed at the solid helium Bragg-peaks.

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