

Undergraduate Research Symposium May 17, 2013 Mary Gates Hall

Online Proceedings

SESSION 1N

MCNAIR SESSION - EXPLORING THE NATURAL WORLD: FROM NUMBERS TO NANOPARTICLES AND BATS TO BACTERIA

Session Moderator: Todd Sperry, Office of Minority Affairs
& Diversity
287 MGH

1:15 PM to 2:45 PM

* Note: Titles in order of presentation.

The Impact of Nucleotide Ratios on Carbon Flux in *Methylobacterium extorquens* AM

Sandy Nguyen, Senior, Microbiology

Mary Gates Scholar, McNair Scholar

Mentor: Mary Lidstrom, Chemical Engineering

Mentor: Norma Cecilia Martinez-Gomez, Microbiology,
Chemical Engineering

Methylotrophic bacteria have long been recognized for their metabolism of reduced single carbon (C_1) compounds. Their potential for biotechnology and the occurrence of C_1 metabolism in all organisms signify their importance on an industrial and fundamental scale. Currently, mechanisms used by methylotrophs to regulate and reset their metabolic network in response to perturbations are not well understood. Previous studies suggest abrupt shifts in nucleotide levels drastically affect growth. This project will examine how nucleotide ratios correlate with carbon flux in *Methylobacterium extorquens* AM1. Once C_1 compounds undergo serial oxidation to formate, carbon flux is partitioned for further oxidation or assimilation. Two reactions involved in C_1 oxidation are known to generate reducing power: (1) the dehydrogenation of methylene-dH₄MPT into methenyl-dH₄MPT catalyzed by MtdA or MtdB and (2) the oxidation of formate into CO₂ catalyzed by Fdh1 or Fdh2. Genetic studies demonstrated differential phenotypes in which *mtdB fdh1* grew similarly to wild type while *mtdB fdh2* grew worse relative to the *mtdB* mutant strain. One possible explanation is a global decrease in NADH production offsets the delicate balance of intracellular nucleotides required for an already reducing power-limited mode of growth. To explore this hypothesis, I will conduct experiments to: (1) quantify the levels of NADP⁺, NADPH,

NAD⁺, and NADH in WT, *mtdB*, *mtdB fdh1*, and *mtdB fdh2* and (2) manipulate nucleotide ratios with overexpression and deletion of the *pntAB* and *udhA* genes. These genes encode for membrane bound (PntAB) and soluble (UdhA) transhydrogenases capable of interconverting between NADPH and NADH. Since mechanisms exist in other bacteria to alter nucleotides pools to meet metabolic demands, a similar mechanism can be predicted to operate in *M. extorquens* AM1. Success in this project will lead to better understanding of how cells balance reducing power and energy for oxidation and growth, ultimately leading to improved biotechnological utilization.

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Rheological Characterization of Polymer Solutions with Nanoparticles

Jordan Kennedy, Junior, Mechanical Engineering, Montana
State University

McNair Scholar

Mentor: Jennifer Brown, Chemical and Biological
Engineering, Montana State University

Xanthan gum (XG), a biopolymer excreted by bacterium *Xanthomanoas campestris*, is used in pharmaceuticals, cosmetics, agricultural products, food products, industrial products, and is used to enhance oil recovery processes because of its properties as a thickening agent, dispersion agent, and stabilizer of emulsions and suspensions. Locust bean gum (LBG), a polymer extracted from the seeds of the carob tree (*Ceratonia siliqua*), is of interest in the biopharmaceutical field as a medium for oral drug delivery. With the addition of nanoparticles, the material properties of the polymer solutions can be significantly altered. Understanding of polymer-

particle interactions and their impact on the material response to shear through rheological measurements is necessary for targeted design of material properties for specific applications. Flow and oscillatory testing was performed on XG and LBG solutions with and without the addition of silica dioxide (SiO₂) nanoparticles. Under constant shear, XG solution shows a shear thinning behavior typical of weak gels. With the addition of nanoparticles, the shear thinning behavior of XG is still present but at an overall higher viscosity. LBG shows shear thinning behavior with a Newtonian region at lower shear rates. The addition of nanoparticles to solution shows a region of shear thickening at lower shear rates and shear thinning behavior at higher shears at a considerable higher overall viscosity than the LBG solution without nanoparticles. When strain is held constant with increasing frequencies, the storage (G') and elastic (G'') modulus show that XG has a tendency of more elastic behavior than LBG. The addition of nanoparticles results in more viscous solutions with a higher elastic response. LBG behavior is more heavily impacted by the addition of SiO₂ nanoparticles than XG.

POSTER SESSION 2

Balcony, Easel 112

12:45 PM to 2:15 PM

Phase Behavior of Dilute Block Copolymer and Protein Mixtures

Alysa Marie Joaquin, Fifth Year, Chemical Engr: Nanosci & Molecular Engr

Mary Gates Scholar

Mentor: Lilo Pozzo, Chemical Engineering

The behavior of polymer/protein mixtures has been widely studied within the framework of depletion forces, a colloidal phenomenon driving the attraction of like-particles due to osmotic pressure. However, the behavior of dilute polymer/protein mixtures is still not fully understood. Ordered protein structures, such as crystals and colloidal clusters, could be achieved by tuning excluded volume interactions through the modification of polymer conformation. The temperature-dependent morphology of block copolymers allows us to fine-tune these depletion interactions. To assess phase behavior in a model system, aqueous mixtures of protein (bovine serum albumin) and block copolymer (PEO_x-PPO_y-PEO_x) have been created. Electrostatic interactions between proteins were screened by adding salt to the mixtures. The dependence of phase behavior on these parameters was determined using UV-Vis spectroscopy to measure turbidity. The morphology and size of protein structures was also evaluated using optical microscopy and dynamic light scattering. Mixtures with higher polymer concentrations displayed an increased propensity to develop turbidity at low temperatures. This effect was mitigated upon reaching the

polymer micellization temperature, whereupon the decreased osmotic pressure reversed protein aggregation, resulting in a clear solution. Defining the conditions required for the formation of ordered protein aggregates in polymer media has valuable implications for biology and medicine. This work represents a step towards determination of the optimum conditions for creating protein crystals suitable for structural proteomics and colloidal clusters for drug-delivery.

POSTER SESSION 2

Balcony, Easel 113

12:45 PM to 2:15 PM

Aqueous Dispersions of Composite Nanoparticles for Polymer Solar Cell Applications

Curtis Liam (Curtis) Whittle, Senior, Chemical Engr:

Nanosci & Molecular Engr

Mentor: Lilo Pozzo, Chemical Engineering

Mentor: Jeffrey Richards, Department of Chemical Engineering

Poly(3-hexylthiophene) (P3HT) and 6,6-phenyl-C60 butyric acid methyl ester (PCBM) are model materials used to study and understand the performance of polymer solar cells. A critical design parameter in improving device performance is the structural morphology of the active layer. Traditional processing of organic solar cells involves the deposition of a P3HT/PCBM composite film from a common solvent and then post-processing treatments (i.e. annealing) to influence the extent of phase segregation and improve the percolation of electron and hole transport pathways throughout the film volume. Therefore, the electronic properties of the resulting solar cells are inherently tied to how the film is processed (e.g. choice of solvent, annealing temperature, film thickness). While process optimization has led to improvements in laboratory performance, it is challenging to extend the same principles to improve the performance of large scale roll-to-roll processes because deposition conditions vary significantly. Increasingly, researchers recognize the need for methods that decouple film processing from active layer structure and device performance. My research involves the synthesis of P3HT/PCBM composite nanoparticles (CNPs) in aqueous dispersion as a means to circumvent the dependence of active layer structure on the specific mode of deposition of the P3HT/PCBM film. I have synthesized CNPs with variable content of P3HT/PCBM and different preparation procedures while also controlling particle size. The characterization of these particles focuses on spectroscopy, small angle X-ray scattering (SAXS), dynamic light scattering and the performance evaluation of devices produced with CNP active layers. This project will tie device performance to CNP structure regardless of active layer processing, and assist in identifying CNPs with optimized morphology without the need for annealing or post-processing.

POSTER SESSION 2

Balcony, Easel 114

12:45 PM to 2:15 PM

Surface Energy of Graphene Determined by Intrinsic Friction Microscopy

Brad Anthony (Brad) Krajina, Senior, Chemical Engineering
Mentor: Rene Overney, Chemical Engineering

The building material of graphite, a two-dimensional material of single atomic width, possesses remarkable electrical, thermal, and mechanical properties. Due to its exceptional properties, research in graphene is actively pursued for applications such as electronics, solar-cell technology, and sensing materials. A critical question is how graphene may be combined with other materials (e.g. polymers) to form unique hybrid materials with novel functional properties. Thereby of great importance is the surface energy of single layer to multilayer graphene. Following this, we are exploring the surface energy of few-atomic-layer graphene as a function of the number of atomic layers present. To this end, we prepared few-atomic-layer graphene materials through a simple technique involving cleaving bulk graphite with tape and transferring the cleaved material to a suitable substrate. Such materials can be readily identified under optical microscope and further characterized by atomic force microscopy (AFM) — a scanning probe technology that provides nano-scale information of materials by probing the surface with a tip of atomic-scale width. After initial topographical identification, the surface energy and friction values of graphene were determined using Intrinsic Friction Analysis (IFA). This technique analyzes energetically the thermally active adhesive modes of interactions between the probing tip and the graphene surface. With knowledge of the surface energy of the probe, the sample surface energy can be deconvoluted from the energy information. We have employed this technique on few-layer graphene materials of multiple thicknesses. Our results reveal an energy-friction iso-line that is representative for planar systems with thermally active internal modes that are restricted to vibrational modes. While we observe for decreasing thickness increasing friction forces, the surface energies are decreasing from bulk graphite of 63 mJ/m² to graphene of 48 mJ/m².

POSTER SESSION 2

Balcony, Easel 117

12:45 PM to 2:15 PM

Molecular Simulations of Single-Chain Organic Photovoltaic Polymers in Various Environments

Melissa C. (Melissa) Gile, Senior, Chemical Engineering, Mathematics
Mentor: Jim Pfaendtner, Chemical Engineering

The purpose of this study is to determine fundamental structure-solvent-property relationships in organic photovoltaic polymers (OPV's), with the overarching goal of increasing the efficiency of OPV's. A typical silicon-based photovoltaic plant outputs approximately 88,000 m² of photovoltaic cells each year- about the size of 16 football fields. On the other hand, an organic photovoltaic printer will produce the same area in up to 10 hours. OPV's are incredibly fast, cheap, and easy to produce relative to their inorganic counterparts, but fall short within the realm of efficiency; the 10% efficiency of OPV's can hardly rival the ~40% efficiency of inorganic photovoltaic technology. If the efficiency of OPV's can be increased, this will have a drastic impact on the competitive marketability of photovoltaic technology. This project aims at developing computational models to study the role of solvents in the self-assembly of polythiophenes during the printing process. These models are generated in GROMACS, a program that uses classical forces such as Coulombic or Van Der Waals forces, to predict how molecules will behave with time. This is problematic, however, for OPV's, as key interactions occur on the quantum level, and new classical force fields, which are computationally very efficient, need to be altered in order to accurately calculate these interactions. A force field is being developed and refined by comparing our computational results with experimental results from the Pozzo Research Group within the Department of Chemical Engineering. Once these results are reliably consistent with each other, we can begin running simulations and gathering data regarding how OPV's assemble in various environments. In particular, this poster explains a systematic methodology I have developed to use the GROMACS program to perform molecular dynamics (MD) simulations of single chain OPV's in various solvents as well as simulations of bulk OPV's in the melt state.

POSTER SESSION 2

Balcony, Easel 111

12:45 PM to 2:15 PM

Interfacially Constrained High Reverse Selective Membrane Material within Nanoporous Systems

Tiep Hoang Pham, Senior, Chemical Engr: Nanosci & Molecular Engr
Mentor: Rene Overney, Chemical Engineering
Mentor: Lakshmi Suhasini Kocherlakota, Chemical Engineering

CO₂ separation from flue gases constitutes to nearly 40% of the CO₂ emission in the United States. Developments resulting from this work address factors key to increasing the transport properties in polymer membrane systems. In particular, this work explores method to engineer porous structure to enhance the selectivity of polymeric membrane. The polymer system of interest in this study is poly(1-trimethylsilyl-

1-propyne) (PTMSP), a glassy polymer of extraordinary high free volume compared to conventional polymers. It is "reverse-selective" for CO₂ separation from flue gases such as nitrogen or hydrogen, i.e., transports CO₂ gas faster in respect to lighter flue gases. Based on prior studies that showed that enhanced transport properties for PTMSP if constrained to thin films, here we present our data for PTMSP if constrained in nanoporous functionalized anopore alumina oxides (AAO) "sieve" membranes. Impregnation was achieved via vacuum solution impregnation. The overall CO₂ permeability of impregnated membranes was found to be ~80,000 Barrer, which is almost two times higher than that of bulk PTMSP membranes. Selectivities of CO₂/Helium and CO₂/Nitrogen in impregnated membranes were found to be ~7.0 and 9.0, respectively; these are also noticeably higher than the corresponding selectivities of 6.0 and 6.6 found in bulk membranes. Furthermore, we investigated the temporal stability of these membranes that are notorious for their fast aging in the form of ultrathin films. The origin for physical aging is the collapse of the free volume. A two week aging study of PTMSP revealed a significantly slowed down physical aging process if confined in nanoporous AAO by about a factor of 20 over thin films. The exposure to the radial constraint within the pores helped stabilize the free volume and reduce the occurrence of free volume collapse.

POSTER SESSION 2

Balcony, Easel 119

12:45 PM to 2:15 PM

Intracellular Trafficking of Toll-Like Receptor 9 (TLR9) Ligands

Melanie Jean Coyne, Junior, Chemical Engineering

Mentor: Hong Shen, Chemical Engineering

Mentor: Helen Chen, chemical engineering

With the proliferation of autoimmune diseases and cancer it is of increasing importance to discover new ways to utilize nanoparticles as carriers for the delivery of therapeutic agents. To achieve this aim, the trafficking of nanoparticles within dendritic cells must be better understood. When cells uptake foreign material, an innate immune response is triggered through the activation of pattern recognition receptors such as toll-like receptor 9 (TLR9). TLR9 ligands follow one of two pathways when introduced into a cell - one trafficking through early endosomes, the other through late endosomes. This research analyzes the intracellular trafficking of TLR9 ligands through the image analysis of dendritic cells. Using an imaging software, ImageJ, it is possible to plot the relative intensities of fluorescently labeled polystyrene nanoparticles coated with TLR9 ligands CpG 2216 or CpG 1826 as well as late endosomal markers Rab7 or LAMP2. By analyzing the co-localization of these intensity profiles, it can be determined if there is recruitment of the late endosomal

marker to the endocytic vesicle of the nanoparticle. The recruitment analysis confirms which intracellular pathway is taken by these nanoparticles. A statistical analysis of a large sample size of nanoparticles will be performed. This research will shed light on how nanoparticles can be used as drug carriers by supplying critical information about the intracellular fate of nanoparticles coated with TLR9 ligands.

POSTER SESSION 2

Balcony, Easel 118

12:45 PM to 2:15 PM

Using Molecular Simulation to Improve the Efficiency of Biomass Processing

Zachary Ryan (Zack) Jarin, Senior, Chemical Engr: Nanosci & Molecular Engr

Mentor: Jim Pfaendtner, Chemical Engineering

Currently, the United States faces an impending energy crisis. To ensure energy security, conversion of biomass to small molecules for use in fuels or chemical processes must become more energy efficient. However, a major hurdle to raising productivity is the robust structure of biomass and subsequent resistance to breakdown. In the past ten years, experiments have shown "ionic liquids," a special group of solvents, dissolve biomass. Unfortunately, these experiments are not guided by molecular scale design principles hindering this promising research. This project focuses on providing the fundamental knowledge to guide and explain the phenomenon by using molecular dynamics (MD) to study the interaction of cellulose and other parts of biomass as a function of solvent environment. This new perspective requires simulated MD in combination with an enhanced sampling method. Enhanced sampling, in this case umbrella sampling, involves applying artificial forces on atoms to cause rare events that would not normally occur on the time scale of molecular scale simulations. Examples of rare events that are challenging to directly observe in MD simulation include chemical reactions, protein folding and unfolding and binding and unbinding of polymers. This work focuses on binding and unbinding events of biomass polymers. To cause the binding and unbinding events, umbrella sampling uses a force similar to a spring to hold a variable like dihedral angles and number of hydrogen bonds constant. Umbrella sampling is a versatile technique and is used on a wide variety of variables but this work uses it to vary the position of the dimer with respect to the cellulose surface. By varying position, the interaction energy is calculated. The interaction energy will give a deeper insight into the mechanism of dissolving biomass while providing a profounder understanding of the fairly new materials, ionic liquids.

SESSION 2G

MICRO- AND NANO-MATERIALS IN ACTION

Session Moderator: John Berg, Chemical Engineering
242 MGH

3:45 PM to 5:15 PM

* Note: Titles in order of presentation.

Rheology of Dense Calcium Carbonate Dispersions

Aaron Joseph (Aaron) Johnson, Senior, Chemical Engineering, Bioresource Science and Engineering
Mary Gates Scholar

Mentor: Kevin Hodgson, Bioresource Science & Engr.
Mentor: John Berg, Chemical Engineering

From the fillers that give body to ordinary paper to the antacids that relieve indigestion, calcium carbonate suspensions play an important role in our day-to-day lives. It is often desirable to work with slurries that contain the highest possible fraction of solids. The goal of this research has been to investigate ways to improve the flow of high solids dispersions of calcium carbonate through the use of rheology modifiers. These are chemicals which, when added in small amounts, allow the dense slurries to flow as easily and smoothly as possible. Improving flow characteristics of high solids dispersions has a huge potential for reducing the amount of energy needed for various processes, such as pumping, coating and de-watering. One very promising modifier has been found to be sodium polyacrylate. Both traditional and new products, like nano-sized calcium carbonate particles, have shown significant improvements using this modifier. In this research, the rheological properties such as the viscosity function and the yield stress are determined as functions of additive amount, volume fraction of solids, and pH of the aqueous dispersion medium. All of these have been shown to important parameters in achieving optimum performance.

SESSION 2G

MICRO- AND NANO-MATERIALS IN ACTION

Session Moderator: John Berg, Chemical Engineering
242 MGH

3:45 PM to 5:15 PM

* Note: Titles in order of presentation.

The Charging of Carbon Black Pigments in Apolar Media

Max Grigorovich Kaganyuk, Senior, Chemical Engineering
Mentor: John Berg, Chemical Engineering
Mentor: Matthew Gacek, Chemical Engineering

Electrophoretic displays, such as the Kindle®, currently employ electrostatic effects in apolar media to create a paper-like display. In an electrophoretic display, images are comprised of black and white pixels generated by applying an electric field to reposition charged pigment particles. The optimization of this technology is limited due to the incomplete knowledge of the mechanism(s) by which particles acquire charge in these systems. My project explores the charging behavior of carbon black pigments dispersed in apolar media. Previous studies of mineral oxide particles have provided support for the theory of an acid-base charging mechanism for particles dispersed in apolar media with various charge stabilizing surfactants. My current work looks at the possible extension of the theory of an acid-base charging mechanism to carbon black pigments in apolar systems. I have investigated the charging behavior of four different carbon black pigments by measuring the electrophoretic mobility of each pigment dispersed in solutions of heptane, and a charge stabilizing surfactant at varying weight percentages. Three surfactants were used for charge stabilization: Aerosol OT, SPAN 80 and OLOA 11000. Aerosol OT is a neutral surfactant in water, whereas SPAN 80 is acidic and OLOA 11000 is basic. The surface characteristics of each carbon black pigment were studied by Inverse Gas Chromatography (IGC) and X-ray Photoelectron Spectroscopy (XPS). The preliminary findings of my investigation show the sign of the charge for the carbon black pigments to be dependent on the charge stabilizing surfactant used.

POSTER SESSION 3

MGH 241, Easel 134

2:30 PM to 4:00 PM

Modeling $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ –

– δ (LSCF) with Nonlinear Electrochemical Impedance Spectroscopy
Stephanie Riemer (Stephanie) Hare, Senior, Chemical Engineering

Mentor: Stuart Adler, Chemical Engineering

Solid Oxide Fuel Cells (SOFCs) are some of the most efficient fuel cells available, but their widespread use is limited by the high operating temperatures they require. New materials and characterization techniques are being investigated to reveal the properties of SOFC electrode materials to make them more feasible commercially. Electrochemical Impedance Spectroscopy (EIS) is a commonly-used analysis tool for the characterization of SOFCs. The technique measures the transient response of a SOFC electrode mate-

rial by passing a sine wave current of specified frequency through the cell, and measuring the amplitude and phase of the cell voltage. When doing simple EIS, only the first harmonic of the response is analyzed, with higher order harmonics ignored. This is done using a linear approximation to describe the mass transfer and kinetics of the material, where these properties are non-linear when rigorously described. Recently workers have begun to explore the use of Nonlinear EIS (NLEIS). By including higher order harmonics, NLEIS seeks to glean significantly more information about the properties of fuel cell electrodes, allowing SOFCs to be more accurately modeled and their efficiency optimized. The goal of my project is to extend existing electrode response models to $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF), a mixed-conducting cathode material of commercial interest. A successful model would have important implications in the alternative energy industry, and allow SOFCs to be a much more viable energy option in the future. My role in this research is to create SOFCs with LSCF as a cathode using simple ceramic firing and "screen printing" techniques to apply a thin electrode layer, and then run NLEIS in order to collect electrochemical data on the electrode. Once this is accomplished, it is expected that LSCF will behave as a combination of the previously studied materials LSC ($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3 - \delta$) and LSF ($\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 - \delta$), however more testing must still be completed.