American Conference on Neutron Scattering

Emerging Applications of Neutron Scattering in Engineering, Arts and Sciences

* Invited Paper

SESSION G03.01: Emerging Applications of Neutron Scattering in Engineering, Arts and Sciences

PM G03.01.01*
Rheo-Small Angle Neutron Scattering Techniques that Leverage Simultaneous Electrical Spectroscopy for the Study of Soft Matter
Jeffrey J. Richards; Northwestern University, United States

Soft matter is a class of materials whose properties arise due to the coupling between the structure and dynamics (i.e., the microstructure) of the material building blocks and transport in and between those structures. Unlike molecular systems, the length scales and time scales relevant to their macroscopic behavior lies in a regime accessible to small angle neutron scattering (SANS) instruments. An emerging challenge in the characterization of soft matter is the measurement of the microstructure far from equilibrium such as in shear flow. In this context, in situ measurements such as Rheo-SANS have become increasingly important to establish the relationship between the microstructure and macroscopic properties. While Rheo-SANS techniques have a strong track record of measuring the structure of soft matter under flow, the dynamics are difficult to access in standard Rheo-SANS measurements. While transient rheological techniques such as LAOS and start-up and cessation experiments have been adapted to be performed simultaneously with SANS measurements, these techniques can be time-consuming and rely on a deep understanding of the material response to the deformation. For the past few years, the NIST Center for Neutron Scattering has been using electrical spectroscopy as a probe of the dynamics of soft matter under flow. This new technique is called Dielectric Rheo-SANS. It combines mechanical and electrical measurements with SANS to provide a flexible platform for the interrogation of structure and dynamics of soft matter out of equilibrium. In this talk, I will demonstrate the use of this technique in a several soft matter systems and discuss the opportunities and its limitations. The talk will focus on our recent work on the response of inverse worm-like micelles to flow. This system exhibits rich structural and dynamic features that evolve in simple shear that can only be understood by coupling all three measurement techniques.

G03.01.02
Investigating Nanoscale Wood-Water Interactions with Neutron Scattering
Nayomi Plaza[1], Sai Venkatesh Pingali[2], Souleymane Diallo[3], Joseph E. Jakes[1] and Donald Stone[4]; [1]Forest Products Laboratory, United States; [2]Oak Ridge National Laboratory, United States; [3]Battelle, United States; [4]University of Wisconsin Madison, United States

Understanding and controlling water in wood is critical to both improving forest products' moisture durability and developing new sustainable forest products-based technologies. While wood is known to be hygroscopic, there is still a lack of fundamental understanding of the nanoscale wood-water interactions that are necessary for increased moisture-durability and dimensional stability. Neutron scattering techniques, such as small-angle neutron

scattering (SANS) and quasielastic neutron scattering (QENS) are suitable to study nanoscale wood-water interactions. They can probe experimentally the nanostructure of both unmodified and chemically modified wood with minimal sample preparation and in situ humidity control. This talk will provide an overview of the basics of neutron scattering of wood and other lignocellulosic materials, as well as the advantages of using these techniques. SANS studies capable of measuring the moisture-induced swelling of wood nanostructure from 1 to 100nm will be discussed. Additionally, QENS studies meant to probe these interactions spatially from 0.3 to 3 nm and temporally in the range of 3 to 400 ps will also be highlighted.

G03.01.03
Using INS to Link Molecular Structure to Materials Properties
Adam Moule[1], Thomas Harrelson[1,2], Makena Dettmann[1], Varuni Dantanarayana[1], Daniel Vong[1], Ty Sours[1], Luke Daemen[3], Ambarish Kulkarni[1], Nir Goldman[4,1] and Roland Faller[1]; [1]University of California, Davis, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Oak Ridge National Laboratory, United States; [4]Lawrence Livermore National Laboratory, United States

The vibrational spectrometer VISION at SNS provides dynamics data from ~1-1000 meV while simultaneously recording a neutron powder diffraction spectrum. We apply the combined use of neutron structure and dynamics data to the study of organic semiconductors (OSCs) and metal organic frameworks (MOFs). For both samples, VISION data enables predictive modeling that cannot be achieved using validation to x-ray diffraction data alone or even combined diffraction/spectroscopy. This is because the INS dynamics data has no selection rules and thus can be partitioned into populations sites in different orientations. Modeling the dynamics spectrum reveals correlated motions that affect materials properties like charge mobility in OSCs and add-molecule binding energy in MOFs. This seminar is designed to be a tutorial for new or recent VISION users to give experience-based advice how to choose/prepare samples, how to approach data simulation, and how to validate simulations to INS data. We also show an early demonstration of materials property prediction. We have explored the use of the empirically corrected density functional tight binding (DFTB) and multi-scale modeling involving molecular dynamics (MD) as approaches to reducing the computational expense of simulating INS spectra. This presentation will quantify the pros and cons of multi-scale approaches by examining both quality of fit to the experimental data and effort in model development.

G03.01.06
Neutron Scattering Analysis of Porosity Changes Associated with Contact Metamorphism of Mancos Shale
Alexis Navarre-Sitchler, Rania Eldam Pommer and Brian Gorman; Colorado School of Mines, United States

Heterogeneity in rock properties, like porosity, can play an important role in geochemical and hydrological processes that control how fluids are transported through and released from rocks and the water-rock interaction that change water composition. The pore structure of rocks is the result of numerous integrated geological processes and pore structure can change though time. Here we investigate the porosity, pore structure, and pore morphology of a marine shale that was metamorphosed by granitic intrusions ~30 million years ago using neutron scattering. Samples of Mancos Shale collected from the East River Valley in southwest Colorado were cut into 150 micron thick wafers and analyzed at the NIST Center for Neutron Research. These data show that metamorphism changes pore anisotropy from elongated in unmetamorphosed rock to more spherical in metamorphosed rock as organic carbon in the marine shale is heated to temperatures greater than 600C. Other associated changes in the rock include: precipitation of pyroxene minerals, increase in unconfined compressive strength, decrease in cation exchange capacity, and decrease in surface area. Taken together these changes in rock properties play an important role in determining the way the East River erodes the bedrock and carves a river channel that is more sinuous with a lower river gradient where rocks are less metamorphosed and less sinuous with a steeper river gradient where the rocks have experienced hornfels grade contact metamorphism.

G03.01.07
Preliminary Investigation of Chinese Jade Sourcing Using Cold Neutron Prompt Gamma Activation Analysis (CNPGAA)
Richard A. Livingston; University of Maryland, United States

Prompt gamma neutron activation (PGAA) is a promising method for elemental analysis of jade artefacts because of its nondestructive mode of operation and its ability to detect the lighter elements including uniquely, hydrogen and boron. To investigate the feasibility of this method several

samples of nephrite [Ca2(Mg, Fe)5Si8O22(OH)2] jade were analyzed. These included geological specimens from four different regions in Asia – Taiwan, Xinjiang and Dunhuang, China, and Siberia – along with a modern replica of a jade dagger made from Wyoming nephrite. The measurements were made at the Cold Neutron PGAA instrument at the NIST Center for Neutron Research. he major nephrite elements - Ca, Mg, Fe and Si - were analyzed with uncertainties in the range of 0.3% -0.4%. The trace elements conventionally used for sourcing nephrite, Cr, Mn and Ni, were analyzed with similar uncertainties. These CPGAA results were in very good agreement with the data from the conventional method for electron microprobe analysis (EMPA) for sourcing nephrite. Modeling of the long-lived residual radioactivity found that it essentially be only 60Co. The activity of the sample with the highest decay rate , the jade blade with 216 Bq at 5 years, is equal to the natural radioactivity emitted by the 40K jn a medium size porcelain vase.

Poster Session: Emerging Applications of Neutron Scattering in Engineering, Arts and Sciences

PG.01.01

The Behavior of Methane and Carbon Dioxide in Small Pores from Producing Intervals of the Middle Devonian Marcellus Shale—Open vs Closed Porosity and the Impact of Mineralogy

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Petroleum (oil and gas) in shale and other tight reservoirs is hosted in organic matter and mineral pores as well as in natural fractures and voids. For thermally mature plays such as the Marcellus Shale, natural gas resources (i.e., methane and other light alkanes) are thought to be primarily contained in organic matter pores with radii <50 nm. Additionally, shale and tight sand reservoirs are attractive candidates for CO_2 enhanced oil recovery (EOR) following primary recovery, and, while these formations are typically thought of as seals for geologic formations where CO_2 can be sequestered, they are also potential targets for geologic CO_2 sequestration. Thus, in order to understand natural gas occurrence, storage, transport, and recoverability within unconventional reservoirs at high thermal maturities, and the potential for CO_2 sequestration within these formations, it is critical to characterize the associated organic matter porosity across length scales from 50 nm down to the angstrom level. Here we present elastic neutron scattering results, using the Near and InterMediate Range Order Diffractometer (NIMROD) instrument at the ISIS Pulsed Neutron and Muon Source, to characterize the behavior of CD_4 and CO_2 within two mineralogically different samples from the same producing interval of the Marcellus Shale. The NIMROD instrument provides structural information on the samples from the atomic regime up to nominal pore radii of ~12.5 nm and, by reaching the CD_4 zero average contrast pressure for both samples (~600 bar) at 60 °C, it is possible to examine the distribution of open versus closed pores within the samples. Our results indicate that only ~10% of the largest pores measured (~12.5 nm) are closed to CD_4 for a quartz-rich sample whereas up to 25% of pores with a nominal radius of ~12.5 nm are inaccessible within a sample with an equivalent proportion of quartz, calcite, and clay. As pore size decreases in both samples the degree of closed porosity increases; all pores with radii ~0.5 nm are effectively inaccessible by CD_4 in both samples. In contrast, no significant differences were observed for CO_2 adsorption between the samples at 22 °C and 40 bar. This suggests that mineralogical variations have little impact on CD_4 and CO_2 adsorption within shales at the dry gas thermal maturation stage, presumably due to the overwhelming abundance of organic porosity within the samples. Furthermore, our results suggest that while most of the methane may be recoverable from shale mesopores (defined by International Union of Pure and Applied Chemistry, IUPAC, nomenclature as pores with diameters between 2-50 nm), essentially all of the shale micropores (IUPAC defined as pores with diameters < 2 nm) are closed to both methane and CO_2. These findings will be discussed in the broader context of evaluating fluid behavior within low permeability geologic matrices and highlight the utility of neutron scattering for such investigations.

PG.01.02

Scattering Study Endorsing the Phase Behaviour Profile of Single and Binary Mixture of PEO-PPO-PEO-Based Block Copolymers in Aqueous Solution

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The present study aims to develop novel polymer micelles/ Polymersoms as nanocarrier for the delivery of hydrophobic drugs, mixture moderately hydrophobic ethylene oxide – propylene oxide – ethylene oxide (PEO-PPO-PEO) triblock copolymers *viz.,* L64, P84, P104 with highly hydrophobic copolymer *viz.,* L61, L81, L101, L121 (each with 10% EO). Moderately hydrophilic polymer showed self-assembly in to spherical core - shell micelles at ambient temperature with growth or transition to rod-like micelles at temperature close to their cloud point (CP). The hydrophobic copolymers in contrast show phase separation with vesicular structure without undergoing micellization. Visual examination of several mixed system and the evaluation of micelle size, shape, aggregation number with Dynamic Light Scattering (DLS) and Small angle neutron scattering (SANS) , it was noticed that the hydrophobic copolymer gets solubilized in the micelles of moderately hydrophobic copolymer showing interesting features depending in their composition and molecular characterization.

PG.01.03

Imaging Fluorescence of He_2* Excimers Created by Neutron Capture in Liquid He II

Xin Wen[1,2,3], Shiran Bao[4,5], Landen McDonald[1,2], Josh Pierce[2], Geoffrey L. Greene[1,2], Lowell Crow[2], Xin Tong[2,6,7], Anthony Mezzacappa[1,2], Ryan Glasby[1], Wei Guo[4,5] and Michael Fitzsimmons[1,2,3]; [1]The University of Tennessee, Knoxville, United States; [2]Oak Ridge National Laboratory, United States; [3]Shull Wollan Center-A Joint Institute for Neutron Sciences, United States; [4]Florida State University, United States; [5]National High Magnetic Field Laboratory, United States; [6]Chinese Academy of Sciences, China; [7]Spallation Neutron Source Science Center, China

High spatial and temporal resolution measurements of flow under extreme Reynolds number (up to ~10^8) conditions have long eluded scientists and engineers. Accepted benchmarks for flow in this regime have been generated from direct numerical simulation (DNS) of individual molecules in fluid flow, however it is necessary to capture canonical, high resolution evidence to validate these models. Liquid He II presents itself as an ideal medium to conduct such research due to its vanishingly small kinematic viscosity, lending well to the creation of incredibly turbulent conditions. We have developed a technique that shows unequivocal evidence for the formation of He_2* excimer tracers in liquid He II created by ionizing radiation produced through neutron capture. Fluorescence is induced in these excimers by high-power laser pulses and is recorded by a camera at a rate of 55.6 Hz. Thermal counter flow techniques are then employed in order to generate flow within the normal component of the liquid He. We have demonstrated the ability to determine the location of a fluorescence event with an uncertainty of 5 microns. The technique enables three-dimensional measurement of turbulence around macroscopic size (liter+) objects or vortex matter that has applications ranging from improving efficiency in transportation to quantum turbulence modeling in cosmology and astrophysics.

PG.01.04

Imaging Fluorescence of *He_2 Excimers Created by Neutron Capture in Liquid He II—A New Approach for Turbulent Flow Research**

Xin Wen[1,2,3], Shiran Bao[4,5], Landen McDonald[1,2], Josh Pierce[2], Geoffrey L. Greene[1,2], Lowell Crow[2], Xin Tong[2], Anthony Mezzacappa[1,2], Ryan Glasby[1], Wei Guo[4,5] and Michael Fitzsimmons[1,2]; [1]The University of Tennessee, Knoxville, United States; [2]Oak Ridge National Laboratory, United States; [3]Shull Wollan Center - a Joint Institute for Neutron Sciences, United States; [4]Florida State University, United States; [5]National High Magnetic Field Laboratory, United States

We show unequivocal evidence for formation of *He_2** excimers in liquid He II created by ionizing radiation produced through neutron capture. Laser beams induced fluorescence of the excimers. The fluorescence was recorded by a camera at a rate of 55.6 Hz with the ability to determine the location of an event with an uncertainty of 5 microns. The technique enables measurement of turbulence around macroscopic size (liter+) objects or vortex matter in three dimensions under conditions of extreme Reynolds number. Using thermal counter flow techniques we explored excimer flow in cryogenic He. Work supported by the Office of Basic Energy Sciences, U.S. Department of Energy, Division of Materials Science and Scientific User Facilities, and ORNL Lab Directed Research and Development, and

support from National High Magnetic Field Laboratory, which is supported by the National Science Foundation.

2. Peetermans, S., et al. "Cold neutron diffraction contrast tomography of polycrystalline material." *Analyst* 139.22 (2014): 5765-5771.

PG.01.05

Trindex—3D Grain Mapping with Time-of-Flight Neutron Imaging

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The mechanical and functional properties of polycrystalline materials have significant contributions from the 3D interaction of grains that form their micro-structure. Such grain maps can be extracted from existing characterisation techniques that utilise neutrons, X-rays or electrons. However, complimentary techniques using neutron imaging, in particular, have not yet developed to maturity. Furthermore, neutrons provide distinct advantages where, due to their lower attenuation, larger materials can be analysed, such as real-world engineering materials.

Here, a novel 3D grain-mapping algorithm using neutron imagine, known as *Trindex*, has been demonstrated to reveal the micro-structure of a prototypical cylindrical iron material. While there already exist several methods on grain mapping with neutron imaging [1,2], *Trindex* provides a robust and relatively straightforward methodology. *Trindex* is a pixel-by-pixel neutron time-of-flight reconstruction method which extracts the morphology of grains throughout the sample, in addition to their pseudo-orientations. Experiments were performed at the SENJU beamline of the Japan Proton Acceleration Research Complex (J-PARC). For the setup, an imaging detector was placed behind the sample with diffraction detectors simultaneously collecting the backscattering from the sample. Such diffraction will be used to confirm grain orientations. Details of the methodology and the resulting 3D grain maps of materials will be presented.

1. Cereser, A., et al. "Time-of-flight three dimensional neutron diffraction in transmission mode for mapping crystal grain structures." *Scientific reports* 7.1 (2017): 1-11.