2016
Accomplishments and Opportunities
ON THE COVER

The NCNR’s neutron source provides a valuable research tool for a wide variety of scientific fields from biological systems, engineering materials, to magnetic structures, and more. The cover features data from only a few of the experiments highlighted in this report.
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I am delighted to present to you this year’s annual report for the NIST Center for Neutron Research, containing a selection of the NCNR’s accomplishments and opportunities for 2016.

It was a very good year for facility operations: the reactor operated at full power for 265 days with 96.5% reliability. Both cold sources operated with excellent reliability.

Two major instrument development efforts – vSANS and CANDOR – were the focus of much effort this past year. With major procurements awarded, extensive site preparation complete, and instrument installation well underway, both instruments are scheduled to deliver first neutrons in 2017. The addition of vSANS and CANDOR to the instrument suite will enable new capabilities for users in terms of speed and flexibility of neutron scattering measurements.

New capabilities for users are not just limited to construction of new instruments. Also reported here is a new capability for the simultaneous measurement of dielectric relaxation and rheology while performing small angle neutron scattering measurements. In addition, the new “octo-strain” and shear device tested last year are now in operation on the BT8 engineering diffractometer. Finally, you will read about a new micro-flow SANS capability that is allowing users to obtain macromolecular structure information with SANS for fluids at extremely high flow rates. Developments such as these result from user input, augment our existing measurement capabilities and advance science. We also collaborate with other neutron facilities in this important aspect of neutron scattering instrumentation.

In September, the University of Maryland and the NCNR hosted over 80 attendees for the 9th International Workshop on Sample Environment at Scattering Facilities. This workshop, which was held at Liberty Mountain near Gettysburg, PA, brought together scientists, engineers, and technicians to exchange experience, form collaborations, and discuss new ideas in this essential component to user facility operations.

As ever, the reason for the NCNR is to enable excellent science that comes from the many researchers who use our facility. You will find many exciting research highlights in the pages that follow. I hope that you enjoy reading them as much as I have.
Neutrons provide a uniquely effective probe of the structure and dynamics of materials ranging from water moving near the surface of proteins to magnetic domains in memory storage materials. The properties of neutrons (outlined below) can be exploited using a variety of measurement techniques to provide information not otherwise available. The positions of atomic nuclei in crystals, especially of those of light atoms, can be determined precisely. Atomic motion can be directly measured and monitored as a function of temperature or pressure. Neutrons are especially sensitive to hydrogen, so that hydrogen motion can be followed in H-storage materials and water flow in fuel cells can be imaged. Residual stresses such as those deep within oil pipelines or in highway trusses can be mapped. Neutron-based measurements contribute to a broad spectrum of activities including engineering, materials development, polymer dynamics, chemical technology, medicine, and physics.

The NCNR’s neutron source provides the intense, conditioned beams of neutrons required for these types of measurements. In addition to the thermal neutron beams from the heavy water moderator, the NCNR has two liquid hydrogen moderators, or cold sources which supply neutrons to three-fourths of the instruments. One is a large area moderator and the other is smaller, but with high brightness.

There are currently 28 experiment stations: 12 are used for neutron physics, analytical chemistry, or imaging, and 16 are beam facilities for neutron scattering research. The subsequent pages provide a schematic description of our instruments. More complete descriptions can be found at www.ncnr.nist.gov/instruments/. Two new cold neutron instruments are under development, including a very small angle neutron scattering instrument (vSANS), and a quasi-white beam neutron reflectometer (CANDOR).

The Center supports important NIST measurement needs, but is also operated as a major national user facility with merit-based access made available to the entire U.S. technological community. Each year, about 2000 research participants from government, industry, and academia from all areas of the country are served by the facility (see pp. 58). Beam time for research to be published in the open literature is without cost to the user, but full operating costs are recovered for proprietary research. Access is gained mainly through a web-based, peer-reviewed proposal system with user time allotted by a beamtime allocation committee twice a year. For details see www.ncnr.nist.gov/beamtime.html. The National Science Foundation and NIST co-fund the Center for High Resolution Neutron Scattering (CHRNS) that currently operates five of the world’s most advanced instruments (see pp. 61). Time on CHRNS instruments is made available through the proposal system. Some access to beam time for collaborative measurements with the NIST science staff can also be arranged on other instruments.

**Why Neutrons?**

Neutrons reveal properties not readily probed by photons or electrons. They are electrically neutral and therefore easily penetrate ordinary matter. They behave like microscopic magnets, propagate as waves, can set particles into motion, losing or gaining energy and momentum in the process, and they can be absorbed with subsequent emission of radiation to uniquely fingerprint chemical elements.

**WAVELENGTHS** – in practice range from ≈ 0.01 nm (thermal) to ≈ 1.5 nm (cold) (1 nm = 10 Å), allowing the formation of observable interference patterns when scattered from structures as small as atoms to as large as biological cells.

**ENERGIES** – of millielectronvolts, the same magnitude as atomic motions. Exchanges of energy as small as nano-electronvolts and as large as tenths of electronvolts can be detected between samples and neutrons, allowing motions in folding proteins, melting glasses and diffusing hydrogen to be measured.

**SELECTIVITY** – in scattering power varies from nucleus to nucleus somewhat randomly. Specific isotopes can stand out from other isotopes of the same kind of atom. Specific light atoms, difficult to observe with X-rays, are revealed by neutrons. Hydrogen, especially, can be distinguished from chemically equivalent deuterium, allowing a variety of powerful contrast techniques.

**MAGNETISM** – makes the neutron sensitive to the magnetic moments of both nuclei and electrons, allowing the structure and behavior of ordinary and exotic magnetic materials to be detailed precisely.

**NEUTRALITY** – of the uncharged neutrons allows them to penetrate deeply without destroying samples, passing through walls that condition a sample’s environment, permitting measurements under extreme conditions of temperature and pressure.

**CAPTURE** – characteristic radiation emanating from specific nuclei capturing incident neutrons can be used to identify and quantify minute amounts of elements in samples as diverse as ancient pottery shards and lake water pollutants.
NIST Center for Neutron Research Instruments (as of December 2016)


[3] BT-2 Neutron Imaging Facility for imaging hydrogenous matter in large components such as water in fuel cells and lubricants in engines, in partnership with General Motors and DOE.

[4] BT-1 Powder Diffractometer with 32 detectors; incident wavelengths of 0.208 nm, 0.154 nm, and 0.159 nm, with resolution up to ∆d/d = 8 x 10^-4.

[5] BT-9 Multi Axis Crystal Spectrometer (MACS II), a cold neutron spectrometer for ultra high sensitivity access to dynamic correlations in condensed matter on length scales from 0.1 nm to 50 nm and energy scales from 2.2 meV to 20 meV.


[7] BT-7 Thermal Triple Axis Spectrometer with large double focusing monochromator and interchangeable analyzer/detectors systems.

[8] VT-5 Thermal Neutron Capture Prompt Gamma-ray Activation Analysis Instrument used for quantitative elemental analysis of bulk materials including highly hydrogenous materials (≅ 1 % H) such as foods, oils, and biological materials.

[9] NG-A Neutron Spin-Echo Spectrometer (NSE) for measuring dynamics from 5 ps to 100 ns.

[10] NG-B 10 m SANS for macromolecular structure measurements.
The Center for High Resolution Neutron Scattering (CHRNS) is a partnership between NIST and the National Science Foundation that develops and operates neutron scattering instrumentation for use by the scientific community. The following instruments are part of the Center: 1 (USANS), 5 (MACS II), 9 (NSE), 11 (NG-B 30m SANS), and 16 (HFBS).

[12] NG-D Cold neutron capture Prompt Gamma Activation Analysis, for quantitative elemental analysis of bulk materials.
[14] NG-D Polarized Beam Reflectometer (PBR) for measuring reflectivities as low as $10^{-8}$ to determine subsurface structure.
[15] NG-2 Backscattering Spectrometer (HFBS) high intensity inelastic scattering instrument with energy resolution < 1 μeV, for studies of motion in molecular and biological systems.
[16] NG-3 VSANS Single measurement investigation of lengths from 1 nm to 2 micron. (installation in progress)
[17] NG-4 Disk Chopper Time-of-Flight Spectrometer for diffusive motions and low energy dynamics. Wavelengths from $\approx 0.18$ nm to 2.0 nm and energy resolutions from $\approx 2$ meV to < 10 μeV.
[18] NG-5 Spin-Polarized Triple Axis Spectrometer (SPINS) using cold neutrons with position sensitive detector capability for high-resolution studies.
[20] NG-5 Precision measurement of the magnetic dipole moment of the neutron.
[21] NG-6 Precision measurement of neutron flux.
[22] NG-6 LAND detector development.
[23] NG-6 Cold Neutron Imaging Facility for imaging hydrogenous matter in large components such as water in fuel cells and lubricants in engines.
[24] NG-7 30 m SANS for microstructure measurements, in partnership with ExxonMobil and University of Minnesota’s IPrime.
[25] NG-7 PHADES Cold neutron test station.
[26] NG-7 Neutron Interferometry and Optics Station with perfect crystal silicon interferometer. A vibration isolation system provides exceptional phase stability and fringe visibility.
[27] NG-7 Neutron Physics Interferometry Test Bed for quantum information science.
[28] NG-7 Horizontal Sample Reflectometer allows reflectivity measurements of free surfaces, liquid/vapor interfaces, as well as polymer coatings.
Dusan Sarenac (U. Waterloo, Canada), Wangchun Chen (UMD/NCNR), and Michael Huber (NCNR) discuss their experiment at PHADES.

James Pressley (U. Pennsylvania) gets assistance loading samples from NCNR’s Grethe Jensen at NGB-30m SANS.

Viacheslav Li (U. Hawaii) is confident that the miniTimeCube neutrino detector is ready to go.

Joshua Graybill and Chandra Shahi (NCNR) at the NG6 Neutron Physics Station, adjusting the electronics for the far UV radiation neutron detector.

NCNR’s Craig Brown explains the science at DCS to Montgomery Blair HS students while Ziling (Ben) Xue and Shelby Stavretis (U. Tennessee Knoxville) collect their data.

NCNR’s Yegor Vekhov and Zhiling Dun (U. Tennessee Knoxville) at DCS, monitoring the dilution refrigerator.
Amber Larson (U. Maryland) collects powder diffraction data from a Hollandite sample at BT1.

Patrick Corona and Nino Ruocco (UCSB) prepare their hydrogel samples for rheo-SANS experiments at NGB-30m SANS.

Boris Khaykovich and Huanui Wu from MIT, and Samuel Richardson (NASA summer intern) are characterizing their latest Wolter optics at the NG6 Cold Neutron Imaging Facility.

At NG7 SANS, NCNR’s Kathryn Krycka and Jeff Krzywon prepare the CCR for Dario Arena and Corisa Kons (U. South Florida) and their study of interfaces of magnetic materials.
The role of molecular complexity in regulating biophysical processes

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Once thought to simply be a passive matrix housing the myriad proteins that carry out the cellular functions necessary for life, the lipid membrane is now understood to play a vital role in those activities. Indeed, the lipid membrane fluidity and flexibility govern a host of processes from the very local diffusion of lipids and proteins that facilitate cell signaling and communication to the large scale deformations that allow red blood cells to flow through small capillaries. At the intermediate scale, collective membrane motions involving tens to hundreds of lipids, such as bending and thickness fluctuations, overlap with the nanometer length scale and nanosecond time scales of protein motions necessary for their activity. Moreover, these mesoscale dynamics are governed by the same elastic properties that determine the energy required for large scale membrane deformations necessary for cell functions such as cell growth and division.

While it is clear that membrane dynamics are essential for biological function, the roles of the numerous components and overall membrane composition in tuning its elastic properties are not well understood. To date, the majority of detailed characterization has focused on model membrane systems composed of a single lipid species of interest to link subtle differences in the lipid chemical structure to changes in the membrane structure and dynamics. Here we gradually increase the complexity of the model system and mix lipids with different tail lengths, dimyristoylphosphatidylcholine (DMPC, 14 carbon tails) and distearoylphosphatidylcholine (DSPC, 18 carbon tails), to study the effects of tail length mismatch and begin to tackle the role of molecular complexity, via lipid composition, on the collective lipid dynamics.

Using neutron spin echo spectroscopy (NSE), we measure both the collective bending and thickness fluctuations in our mixed lipids membranes (Fig 1). The NSE decay constants, Γ, for a fluid bilayer composed of an equimolar mixture of DMPC and DSPC are shown in Fig. 2. For a mixture of protiated lipids in D₂O, the data show a q² dependence as predicted for membranes undergoing bending fluctuations, and the slope is then related to the bending modulus, \( \kappa \) [1,2]. The membrane bending modulus, \( \kappa \), is arguably one of the most important biophysical constants that characterizes the stiffness of lipid membranes and the energetic cost of large-scale deformations of the membrane, such as the formation of highly curved structures necessary for endocytosis as cells take in nutrients. Remarkably, our NSE results demonstrate that \( \kappa \) can be tuned by simply mixing lipids with different tail lengths. As seen in Fig. 3a, the mixed lipid bilayers are softer (lower \( \kappa \)) than either of the pure component membranes.

To experimentally highlight the contribution of thickness fluctuation dynamics in NSE, the lipid tails were contrast matched to the surrounding solvent, emphasizing the collective dynamics of the headgroups. The thickness fluctuations are then seen as a peak in the plot of \( \Gamma \) versus \( q \) (Fig. 2), with the peak width being related to the amplitude of the thickness fluctuations. Once again, we find that the membrane dynamics are highly dependent on the lipid composition, (Fig. 3b) as the amplitude of the fluctuations in each of the pure component membranes are approximately equal, but less than in the mixed lipid bilayers [1,2].

Theoretical and computational studies have suggested that the thickness fluctuation amplitude, \( \sigma_t = \Delta d/d_t \), in which \( d_t \) is the thickness of the hydrophobic tail region, is related to another elastic property of the membrane: the area compressibility modulus, \( K_A \). Assuming that the bilayer volume compressibility is much smaller than the area compressibility (i.e. \( \Delta V/V \ll \Delta A/A \) ) the amplitude is given by \( \sigma^2_t = k_B T K_A A_0 \) [3]. In this expression, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( A_0 \) is the area per lipid headgroup. In other words, the amplitude will be large when \( K_A \) is low and it is easier to compress the membrane laterally.

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Importantly, $K_A$ is also directly related to the bending modulus, $\kappa$, through the well-established expression: $\kappa \propto d^2 K_A$.\[4\]. This relationship implies that the membrane will be softer and easier to bend when $K_A$ is low.

Therefore, the enhanced dynamics in the mixed lipid bilayers seen as a reduction in $\kappa$ and increase in $\sigma_d$ are most likely due to a reduction in $K_A$ upon mixing lipids with different acyl chain lengths. These results suggest that the hydrophobic mismatch between the different tail lengths leads to less efficient lipid packing and increases the area per molecule compared to a single component bilayer, allowing the mixed bilayers to stretch and compress more easily in the lateral direction and ultimately making the membrane more dynamic.

Thus, using the unique ability of NSE to measure both the bending and thickness fluctuations, we were able to explicitly relate an enhancement in the dynamics to a reduction in the area expansion modulus and ultimately differences in the membrane structure upon mixing lipids with different acyl chain lengths. These results highlight the importance of lipid composition in tailoring the membrane properties with important implications for understanding the role of lipid diversity in tuning cell functions. Indeed, a single membrane may contain thousands of different lipid molecules, varying in hydrophilic headgroup structure, charge, glycosylation and hydrophobic tail length, number, saturation and asymmetry, with more than 40,000 chemically distinct lipid molecules identified to date\[5\].

**References**

Neutron reflectometry studies of membrane-bound tubulin reveal an amphipathic helical binding motif

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Bilayer lipid membranes (BLMs) form barriers that separate the interior from the exterior of the cell and divide the cell into specialized compartments called organelles. Proteins that are embedded into BLMs, known as membrane proteins, play diverse roles, including the transportation of various ions, metabolites, proteins, DNA, etc., across the BLMs, thus providing communication pathways between cells and between organelles inside cells. This function is so crucial for health and disease that while membrane proteins account for about 20% of known proteins [1], they comprise 70% of known drug targets [2]. In humans, mitochondria are the organelles responsible for energy conversion, with two main purposes: to store energy, and to produce heat that maintains body temperature. However, mitochondria themselves are also the sources of the reactive oxygen species that damage mitochondria, mitochondrial DNA, and other cellular components. Therefore, maintaining the appropriate conditions that provide sufficient energy for cellular functions and limit the production of chemically damaging reactive oxygen species is crucial for cell life and death. Recent evidence indicates that the regulation of this equilibrium is accomplished at least in part by a complex of the mitochondrial voltage-dependent anion channel (VDAC), a passive transport channel of the mitochondrial outer membrane (MOM), and dimeric tubulin [3], which is best known as a structural protein in microtubules. The association of tubulin with the MOM is particularly suggestive given the role of microtubule-targeting drugs (MTDs) in chemotherapy [4]. In this work we shed light on the role of dimeric tubulin in regulating mitochondrial bioenergetics by investigating the binding of tubulin to biomimetic mitochondrial membranes using a combination of neutron reflectometry (NR) and molecular dynamics (MD) simulations [5].

Tubulin is a heterodimer comprising α and β subunits, which have similar spatial arrangements but different amino acid sequences. In microtubules, the exposed end is always the β subunit; as a result, all MTDs bind to the β subunit [4]. Remarkably, in an in vitro system the rate of interaction between tubulin and a single VDAC channel was observed to depend strongly on the lipid composition of the BLM in which VDAC was embedded. In particular, the interaction rate increased by two orders of magnitude if a lamellar (i.e., preferring a flat membrane geometry) dioleoylphosphatidylcholine (DOPC) membrane was replaced with the non-lamellar (preferring a curved membrane geometry) dioleoylphosphatidylethanolamine (DOPE) [6], suggesting that tubulin is able to distinguish between these two lipid species. Furthermore, these results indicate that the first step of the VDAC-tubulin interaction involves tubulin binding to the lipid membrane surface.

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In this study, we determined the orientation of membrane-bound tubulin—and hence the face of the tubulin molecule that is in contact with the membrane surface—by NR on sparsely tethered BLMs (stBLMs). NR reports on the depth profile of the interfacial components, including the stBLM and any membrane-bound tubulin (Figure 1a). Thus, NR is well suited to determine the spatial extent of the protein in and away from the BLM and yields a potential family of binding surfaces to be investigated by computational methods and amino acid sequence analysis.

For these experiments, an stBLM was composed of a 1:1 molar ratio of DOPC:DOPE. This lipid composition closely mimics the mitochondrial outer membrane, in which the ratio of PC to PE headgroups is about 3:2. The stBLM was bathed in an aqueous 1 mol/L KCl solution buffered at pH 7.4 by 5 mM HEPES. The reflectivity of the stBLM was measured using 4.75 Å neutrons on the NCNR NG7 horizontal reflectometer. To provide contrast between the various components of the stBLM system, a sequence of reflectometry measurements was performed using buffers in 100 % D$_2$O, 100 % H$_2$O, and a 2:1 D$_2$O:H$_2$O mixture. This procedure was then repeated in the presence of 600 nM tubulin dimers (a physiologically relevant concentration).

The reflectivity data (Figure 1b) were then fit to an stBLM model (Figure 2a). Because it accounts for known molecular volumes, molecular connectivity, and stoichiometric constraints, the model is highly constrained. To determine the orientation of the tubulin dimer on the membrane substrate, the expected scattering profile was calculated for various Euler rotations of the known X-ray crystal structure of tubulin. Due to the elongated geometry of the tubulin dimer, the NR profile is very sensitive to the tilt angle $\beta$ (Figure 2b), allowing a precise determination of this tilt angle, $\approx 60^\circ$, from the optimization of the experimental NR data to the stBLM/tubulin model.

To complement the NR results, molecular dynamics simulations were performed to confirm the orientation of $\alpha$-tubulin on a DOPE membrane. A range of possible orientations were evaluated using a coarse-grained model of the protein; likely orientations were then optimized using atomistic simulations. The tilt angle of the tubulin on the membrane surface is consistent with that observed by NR, while the atomistic nature of the simulations allows us to identify the particular domain of the tubulin protein that is responsible for binding to the membrane surface. A comparison of the MD and NR results is shown in Figure 2b.

The binding sequence is shown in green in Figure 2b. Notably, it is on the $\alpha$-tubulin subunit, rather than on the $\beta$-tubulin subunit which is conventionally targeted by chemotherapeutics. When associated with the membrane, this amino acid sequence likely adopts an $\alpha$-helical structure which has opposing hydrophobic and hydrophilic faces, i.e. an amphipathic helix. Such helices are oriented at the interface between the polar lipid headgroups and the hydrophobic lipid tails. We have also shown [5] that the affinity of this helix to the mixed PC/PE membranes considered here depends strongly on the amount of PE lipid. This suggests that the lipid composition of the mitochondrial outer membrane could regulate tubulin binding, which in turn modulates VDAC permeability and consequently mitochondrial function. We hypothesize that this selectivity for the uncharged PE lipids may have developed to overcome electrostatic repulsion between the negatively charged components of the mitochondrial outer membrane and the tubulin molecule.

References

The use of hydrogen as a fuel in light-duty vehicles would offer a significantly cleaner alternative to gasoline, natural gas, or electric, grid-powered vehicles. However, the low energy density of gaseous hydrogen currently requires storage at very high pressures in order to achieve reasonable driving ranges. An alternative to this method is to store hydrogen at lower pressures in a porous adsorbent, in which the hydrogen interactions with the internal surfaces of the material result in a higher density of stored hydrogen than for pure compression to the same pressure.

One class of porous materials that has been well studied for hydrogen storage is metal-organic frameworks (MOFs). These three-dimensional materials are built of metal ions connected by tunable organic linkers, which facilitates the installation of highly selective functionalities into the framework pores and hence the design of structures tuned for specific applications. For hydrogen storage, the incorporation of metal centers with open coordination sites can lead to strong affinities for hydrogen and enhanced storage densities, as the positively charged metal centers strongly interact with guest hydrogen molecules [1-3]. However, the most promising metal-organic frameworks still fall short of the Department of Energy hydrogen storage targets. Therefore, new adsorbents must be designed with an even higher density of open metal coordination sites in order to meet these targets. Using gas dosing in powder neutron diffraction experiments, we were able to demonstrate, for the first time, the interaction of two hydrogen molecules with a single metal center in a metal-organic framework.

We have recently reported the storage of hydrogen in the MOF known as Mn$_2$(dsbdc) (where the organic ligand is dsbdc$^{4-}$ = 2,5-disulfido-1,4-benzenedicarboxylate and Mn stands for manganese). While the organic linker used here is similar to that used to generate the well-studied M$_2$(dobdc) series (dobdc$^{4-}$ = 2,5-dioxo-1,4-benzenedicarboxylate), this material has a unique structure in which the pores exhibit infinite chains of manganese ions, wherein every other manganese is bound by framework organic ligands and two removable solvent molecules. Upon heating the material under vacuum, it is possible to remove these solvent molecules and expose two open sites at the metal capable of binding hydrogen, which we were able to confirm through neutron diffraction (Figure 1) and inelastic neutron scattering experiments (Figure 2).

The hydrogen storage properties of this material were measured via hydrogen adsorption experiments carried out at 77 K and 87 K. The isotherms resulting from these measurements were fit with the dual-site Langmuir model to determine the heat of adsorption of hydrogen in the structure, which was found to be –6.5 kJ/mol for all measured loadings.

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While this value of the binding enthalpy is not quite as large as those exhibited by other MOFs, the advantage of this material is that it can bind two hydrogen molecules per manganese center, as verified by powder neutron diffraction experiments. In order to facilitate these measurements, it was necessary to use an isotope of hydrogen, namely deuterium ($D_2$), which was introduced into the material at loadings of $0.7 \text{ } D_2$ and $1.4 \text{ } D_2$ per metal center. The manganese–$D_2$ distances were found to be $3.40(4) \text{ Å}$ and $3.07(3) \text{ Å}$, respectively, and these distances correspond to a binding strength of $–5.6 \text{ kJ}$ per molar equivalent of $D_2$ as found in the hydrogen adsorption experiments. Furthermore, we used inelastic neutron scattering to characterize $\text{Mn}_2(\text{dsbdc})$ dosed with $\text{H}_2$ and confirmed that the two $\text{H}_2$ molecules are indeed binding to the metal center. Figure 2 illustrates that the rotational spectrum for adsorbed hydrogen is somewhat perturbed from the free-rotor value of 14.7 meV [4]. More importantly, the spectrum is scalable from low coverage to well above 1.4 $\text{H}_2$ per Mn indicating that the two hydrogens are similarly perturbed when adsorbed at this open-Mn.

We additionally sought to demonstrate that the binding of multiple gas molecules to the metal centers extends beyond $\text{H}_2$. Using X-ray and powder neutron diffraction, respectively, we found that samples of $\text{Mn}_2(\text{dsbdc})$ dosed with $\text{CD}_4$ (the deuterium analogue of methane) and $\text{CO}_2$ showed similar gas binding at the open metal coordination sites as with $D_2$.

The applicability of this strategy to a variety of different gas molecules demonstrates its viability and promise as a long-term strategy for increasing the density of gas molecules bound in the pores of metal-organic frameworks. Importantly, these neutron diffraction and inelastic neutron scattering results demonstrate the interaction of two hydrogen molecules with a single metal center in a MOF for the very first time [5]. This is a step toward significantly increasing both the binding enthalpy and storage density of $\text{H}_2$ in porous materials to levels approaching the DOE targets for onboard hydrogen storage in fuel cell vehicles.

References

A variety of economic and environmental factors have sparked interest in the use of natural gas, composed primarily of methane (CH$_4$), as an alternative transportation fuel to petroleum. However, its use in on-board vehicular applications is severely limited by its relatively low volumetric energy density. The development of adsorption-based systems where high surface area materials store large volumes of CH$_4$ at ambient conditions would allow for the use of smaller, lightweight tanks that could be integrated into smaller vehicles such as passenger cars. Metal-organic frameworks (MOFs) have attracted substantial attention as materials for these types of adsorption applications due to their high surface areas and chemically tunable pore dimensions and surface functionality. It has been shown through multiple adsorption studies that Cu$_3$(btc)$_2$ (btc$^-_3$ = 1,3,5-benzenetricarboxylate; HKUST-1) exhibits one of the highest volumetric capacities for CH$_4$ in a MOF at 35 bar and 25 °C [1, 2]. Its structure consists of binuclear copper(II) paddlewheel units connected through the carboxylate linkers to form a three-dimensional pore structure. An axial water molecule on each Cu$^{2+}$ ion can be removed to leave an open coordination site that can attract different gas molecules. The pore structure contains three distinct types of cavities: two large pores with diameters of about 11 Å and 13 Å, which contain the open Cu$^{2+}$ sites exposed to the pore surface; and an octahedral cage (diameter = 5 Å) accessible through triangular windows from the largest pore. An isostructural Cr analog can be synthesized that displays a slightly higher surface area and interesting adsorption behavior for gases such as H$_2$, O$_2$, and CO$_2$, but has yet to be investigated for CH$_4$ uptake.

Correlating structural features with adsorption behavior is a critical part of the evaluation of adsorptive materials and must be accomplished using a variety of experimental techniques. Powder diffraction experiments have been used to determine binding sites for many gas molecules in MOFs, including CH$_4$ in Cu$_3$(btc)$_2$ [3, 4]. These studies have determined that CH$_4$ adsorption occurs in both the octahedral cages and at the open metal sites; however, the data in these reports did not clearly identify the relative affinity, or order of filling, of these sites. It is of particular interest to determine whether the CH$_4$ molecule prefers a perfectly sized cage to enhance adsorbate–adsorbent contacts or an enhanced electronic interaction at an open metal coordination site, or if these structural characteristics are of relatively equal importance. Furthermore, any differences found in the adsorptive behavior of Cu$_3$(btc)$_2$ and Cr$_3$(btc)$_2$ would clarify the nature of the CH$_4$–open metal site interaction. Additional computational studies of adsorption in MOFs can assist in explaining experimental observations and build on experimental foundation to predict adsorptive behavior in other materials. These theoretical studies have become an extremely important tool to guide synthetic efforts in the design of porous materials, as once adsorptive behavior can be adequately predicted entire libraries of thousands of possible structures can be screened for their properties to expose beneficial structural features.

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Neutron diffraction structures were determined at various loadings of CD$_4$ in Cu$_3$(btc)$_2$ and Cr$_3$(btc)$_2$. Data analysis indicated that the initial adsorption site is at the windows to the octahedral cages in both Cu$_3$(btc)$_2$ and Cr$_3$(btc)$_2$. With increased dosing to 1.5 CD$_4$ per metal atom, additional nuclear density was found inside the octahedral cages and at the metal sites in a similar fashion for both materials. At the highest dose of 2.2 CD$_4$ per metal atom, the first three binding sites described above are fully occupied, and a fourth site begins to populate in the 11 Å diameter pore. This site is located above the outside of the ligands that form the surface of the octahedral cages and essentially represents the filling of the surface of one of the large pores (Figure 1).

The major conclusions evident from the combination of the adsorption and diffraction data are that adsorption mechanisms are essentially identical for Cu$_3$(btc)$_2$ and Cr$_3$(btc)$_2$, and that the binding sites in and around the octahedral cage are favored over both metal sites. We infer that the main reason Cu$_3$(btc)$_2$ has a slightly higher volumetric uptake compared to Cr$_3$(btc)$_2$ is due to its slightly smaller unit cell. It is not immediately clear why CH$_4$ adsorption occurs first at the octahedral cage and window sites, rather than at the metal sites as is perhaps expected. In an effort to better understand the origins of this surprising sequential filling of adsorption sites, a detailed computational analysis was performed for CH$_4$ binding in Cr$_3$(btc)$_2$ and Cu$_3$(btc)$_2$.

Binding energies for CH$_4$ were determined by periodic DFT calculations at the window and metal sites and converted to binding enthalpies by applying harmonic vibrational corrections. The calculated difference in energy between the window and metal sites is consistent with the observation in our NPD results that the window sites are occupied first. We hypothesized that the strength of CH$_4$ binding at the Cu$_2^+$ sites might be effectively increased by intermolecular interactions with CH$_4$ molecules already adsorbed at the nearby window sites. The effect of lateral CH$_4$–CH$_4$ interactions has been shown by other researchers to be important given that CH$_4$–CH$_4$ distances are quite short in this topology. Recomputing the binding energy at the metal site and decomposing the interactions between the CH$_4$ molecules reveals that the presence of one CH$_4$ alone increases the binding strength by −1.28 kJ/mol. However, if the structures of both CH$_4$ molecules are allowed to relax, as opposed to only the CH$_4$ at the metal site, binding at the metal site increases further leading to an enhancement of −5.49 kJ/mol (or −2.74 kJ/mol per CH$_4$).

Furthermore, at the configuration from NPD with the highest loading, the CH$_4$ at the metal site interacts with not one but eight CH$_4$ molecules. While the absolute value of this energy should be thought of as a rough approximation, this result emphasizes the importance of the cumulative effect of interactions between neighboring CH$_4$ molecules. Due to these interactions, the effective binding energy at the metal site is not that different from the binding energy at the window site, further explaining why a dual-site Langmuir isotherm was not necessary to fit the adsorption data.

Total volumetric CH$_4$ adsorption isotherms computed with grand canonical Monte Carlo (GCMC) describe the experimental isotherms presented above very well (Figure 2). We extended these calculations to evaluate CH$_4$ adsorption in some structural variations of Cu$_3$(btc)$_2$ and Cr$_3$(btc)$_2$ to gain insight into the possibility of developing an improved adsorbent. We found that while binding enthalpies are increased by ligand substitution, deliverable capacity decreases in all cases from the non-functionalized materials. Additionally, even if we could artificially increase or decrease the heat of adsorption as much as 6 kJ/mol, there is no significant increase in the deliverable capacity beyond what is calculated for the actual Cu$_3$(btc)$_2$ structure. In other words, Cu$_3$(btc)$_2$ already has the ideal binding enthalpy required to maximize the deliverable capacity.

To date, Cu$_3$(btc)$_2$ has shown the most promise of any MOF as a CH$_4$ storage material for relevant industrial applications. In this work, we have carried out a thorough investigation regarding the underlying mechanistic reasons for its high volumetric uptake, combining several types of experimental and computational data. The fact that enhancement of CH$_4$ binding at its open metal site is mostly due to CH$_4$–CH$_4$ interactions between adjacent adsorbed molecules is a very important conclusion that should assist future research into new materials for this application. The structure of Cu$_3$(btc)$_2$ has just the right combination of features to maximize both CH$_4$–framework and CH$_4$–CH$_4$ interactions for optimum delivery capacity. Furthermore, this work highlights the level of mechanistic understanding that can be achieved when experimental and computational techniques are combined. This approach is currently being expanded to other adsorption applications in other MOF systems.

References

Enhancements in superionic conduction properties in Lithium and Sodium closo-dodecaborate salts via substitutonal and morphological modifications

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Finding replacement solid-state electrolytes with sufficiently high conductivities and stabilities are the elusive answer to the inherent shortcomings of organic liquid electrolytes prevalent in today’s rechargeable batteries. We recently found that solid sodium and lithium salts of the divalent icosahedral B₁₂H₁₂²⁻ anion, indeed, possess the requisite (super)ionic conductivities comparable to liquid electrolytes, but only above their high order-disorder phase transition temperatures near 530 K and 620 K, respectively. Making them more applicable to future solid-state-battery technologies requires much lower transition temperatures closer to ambient operating temperatures. We have been able to accomplish this in two different ways: (i) by replacing the B₁₂H₁₂²⁻ anions with chemically modified monovalent CB₁₁H₁₂⁻ anions [1] (see Fig. 1) and (ii) by ball-milling the salts to generate nanosized disordered crystallite morphologies [2].

Neutron scattering methods were used to characterize the various structures as well as the high anion reorientational mobilities in the disordered superionic phases. These high mobilities are believed to facilitate rapid cation diffusive motions through the interstitial channels of these materials. The 4 K neutron vibrational spectra from FANS for ordered NaCB₁₁H₁₂ and LiCB₁₁H₁₂ shown in Fig. 2a are in good agreement with the DFT-simulated phonon densities of states (PDOS) of the orthorhombic structures determined by diffraction. As suggested by the simulated PDOS of the isolated CB₁₁H₁₂⁻ anion, the neutron vibrational spectrum is clearly sensitive to the structural arrangement.

Figure 1 shows the ionic conductivity data for the modified NaCB₁₁H₁₂ and LiCB₁₁H₁₂ salts and ball-milled Na₂B₁₂H₁₂ compared with those for pristine Na₂B₁₂H₁₂ and Li₂B₁₂H₁₂. NaCB₁₁H₁₂ and LiCB₁₁H₁₂ display dramatically lower respective superionic transition temperatures near 380 K and 400 K and order-of-magnitude higher conductivities compared to their divalent-anion cousins. Moreover, ball-milled Na₂B₁₂H₁₂ (unlike pristine Na₂B₁₂H₁₂) maintains superionic conductivity well below 530 K down to room temperature.

FIGURE 1: Ionic conductivities for NaCB₁₁H₁₂, LiCB₁₁H₁₂, and ball-milled Na₂B₁₂H₁₂ compared with those for pristine Na₂B₁₂H₁₂ and Li₂B₁₂H₁₂. Adapted from [1, 3].

FIGURE 2: (a) Neutron vibrational spectra (black) of NaCB₁₁H₁₂ and LiCB₁₁H₁₂ at 4 K compared to the simulated one-phonon (gray) and one+two-phonon (red) densities of states from the DFT-optimized orthorhombic structures (red), and the isolated CB₁₁H₁₂⁻ anion (blue). (b) QENS spectra from DCS with 4.1 Å neutrons (Q = 1.35 Å⁻¹) showing the anion-reorientationally-induced broadening in red for NaCB₁₁H₁₂ (at 375 K) and LiCB₁₁H₁₂ (at 433 K) compared to the resolution-limited elastic-scattering peaks in black observed at 200 K, below the order-disorder phase transitions. (N.B., lower instrumental resolution was used for LiCB₁₁H₁₂)

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Preliminary QENS measurements for natural-boron NaCB$_{11}$H$_{12}$ and LiCB$_{11}$H$_{12}$ confirm orders of magnitude jumps in anion orientational mobilities to between 10$^{10}$ and 10$^{11}$ reorientational jumps s$^{-1}$ in the disordered phases, as reflected in Fig. 2b by the transformation from purely resolution-limited elastic component peaks at 200 K to ones with significant quasielastic broadening at 433 K and 375 K, respectively. For both materials, the observed fraction of scattering that is quasielastic above $Q = 1$ Å$^{-1}$ appears to be of the order of 0.8 or more, suggesting that we are observing anion small-angle-jump reorientations akin to that observed for Na$_2$B$_{12}$H$_{12}$ [3] which is thought to entail a distribution of individual anion motions ranging from one-axis to multi-axis reorientations. The quasielastic linewidths suggest that the monovalent anions are on the order of 60 % more mobile than their divalent analogs. Such higher relative CB$_{11}$H$_{12}$ reorientational mobilities compared to B$_{12}$H$_{12}$ are likely a consequence of relatively weaker cation-anion (Coulombic) interactions as well as, on average, one-half fewer near-neighbor cations for the CB$_{11}$H$_{12}$ anion.

For ball-milled Na$_2$B$_{12}$H$_{12}$, in agreement with the conductivity data in Fig. 1, both X-ray and neutron powder diffraction confirm the stabilization of the disordered superionic pseudo-bcc phase down to at least 5 K. Neutron fixed-window scans (FWSs) and QENS measurements for pre- and post-ball-milled Na$_2^{11}$B$_{12}$H$_{12}$ are shown in Fig. 3. The FWSs in Fig. 3a reflect B$_{12}$H$_{12}$ anion reorientational jump frequencies on the order of 10$^8$ s$^{-1}$ already by ~ 240 K to 250 K after ball-milling (as evidenced by the onset of significant intensity dropoff), which is consistent with the observed presence of the superionic phase.

In comparison, pristine Na$_2$B$_{12}$H$_{12}$ displays hysteretic FWS behavior and high reorientational mobility only at considerably higher temperatures. QENS spectra of ball-milled Na$_2$B$_{12}$H$_{12}$ were measured between 270 K and 400 K and could be fit to a primary Lorentzian component linewidth ($2\Delta$/$\tau_1$) ranging between 0.27 μeV and 11 μeV fwhm, respectively. This narrow Lorentzian component dominated at lower $Q$ values, with increasing contributions from one and probably more broader Lorentzian components at larger $Q$ values, which is again compatible with a small-angle jump mechanism [3]. Anion reorientational jump correlation frequencies derived from the QENS spectral broadening (Fig. 3b) are in excellent agreement with the Arrhenius dependence observed for pristine Na$_2$B$_{12}$H$_{12}$ above its phase transition at higher temperatures. Combined data yield an activation energy for reorientation of 270(3) meV, the same value obtained for pristine bcc Na$_2$B$_{12}$H$_{12}$ from NMR measurements.

The measured elastic fraction of the total QENS spectrum (i.e., the elastic incoherent structure factor, EISF) at 400 K at 0.84 Å$^{-1}$ (using DCS with 11 μeV resolution) was estimated to be $\approx 0.48$. Assuming a similar reorientational mechanism as for pristine disordered Na$_2$B$_{12}$H$_{12}$ [3] this EISF value is consistent with 20 % to 25 % of the anions being relatively immobile in an ordered monoclinic phase at this temperature. Moreover the continued decrease in the FWS in Fig. 3a upon heating above 340 K indicates that this remaining "immobile" phase fraction converts to the superionic phase over a broad temperature range until its completion above 500 K. This transitioning fraction is reversible, as evidenced by the observed hysteretic FWS cooling behavior.

Looking forward, we are exploring analogous chemical and morphological modifications of related Na$_2$B$_{10}$H$_{10}$ and Li$_2$B$_{10}$H$_{10}$ anion-cluster salts and their effects on transition temperatures, anion reorientational mobilities and mechanisms, and resulting cation mobilities as well as molecular dynamics studies to understand the possible link between these orientational anion motions and the observed superionic conductivity.

References
Due to the worldwide demand for plastic, ethylene (C\(_2\)H\(_4\)) is the most widely produced organic compound in the world, with well over 100 million tons of it manufactured each year, largely by refining crude oil. Newly made ethylene is not pure enough to make polyethylene because the refinement process also creates a substantial amount of acetylene (C\(_2\)H\(_2\)), which can poison the catalysts used in the polymerization process. The conventional industrial solution is to convert the undesirable acetylene into ethylene, but this step requires the use of palladium as a catalyst and consumes a significant amount of energy. A promising alternative technology is to use porous adsorbent materials to capture acetylene from ethylene.

We recently discovered that a subfamily of metal-organic frameworks (MOFs) called “SIFSIX MOFs” can effectively remove the contaminant acetylene from ethylene, with unprecedented C\(_2\)H\(_2\) adsorption capacity and C\(_2\)H\(_2\)/C\(_2\)H\(_4\) selectivity [1].

SIFSIX MOFs are comprised of metal ions (e.g., Cu\(^{2+}\), Zn\(^{2+}\) etc.), pyridine-containing organic linkers, and preformed SiF\(_6^{2-}\) (hexafluorosilicate, SIFSIX). In Figure 1, the building units and the crystal structure of a prototypical SIFSIX compound, SIFSIX-1-Cu (1 = 4,4’-bipyridine), is shown schematically as an example. The metal ions coordinate with pyridine in the organic linkers, forming 2-D square grid layers (parallel to crystallographic a-b plane). Along crystallographic c-axis, the SiF\(_6\) units coordinate with the metal ion and function as pillars between the 2-D metal-organic grids, resulting in 3-D extended framework structures. SIFSIX MOFs are highly versatile: by changing the length of the organic linkers, the metal node, and/or framework interpenetration, the pore sizes within this family of materials can be systematically tuned.

Several SIFSIX MOFs, including SIFSIX-1-Cu, SIFSIX-2-Cu (2 = 4,4’-dipyridylacetylene), SIFSIX-2-Cu-i (i = interpenetrated), SIFSIX-3-Ni (3 = pyrazine), and SIFSIX-3-Zn, were investigated for C\(_2\)H\(_2\) capture. First, the C\(_2\)H\(_2\) adsorption isotherm was measured in order to understand the exceptional C\(_2\)H\(_2\) adsorption in these materials, we conducted detailed first-principles DFT-D (dispersion-corrected density-functional theory) calculations. In SIFSIX-1-Cu, C\(_2\)H\(_2\) molecules are bound through strong C-H•••F hydrogen (H) bonding and van der Waals (vdW) interactions with the 4,4’-bipyridine linkers (Fig. 2). The DFT-D calculated static adsorption energy (\(\Delta E\)) is 44.6 kJ/mol. Each unit cell of SIFSIX-1-Cu contains four equivalent exposed F atoms and each exposed F atom binds one C\(_2\)H\(_2\) molecule. The distance between neighboring adsorbed C\(_2\)H\(_2\) is ideal for them to synergistically interact with each other through multiple H\(^{\delta+}\)•••C\(^{\delta-}\) dipole-dipole interactions, further enhancing the energy of adsorption. As four C\(_2\)H\(_2\) molecules are adsorbed per unit cell, the \(\Delta E\) of C\(_2\)H\(_2\) increases to 47.0 kJ/mol. The strong binding of C\(_2\)H\(_2\) at F atoms and the geometric arrangement of SiF\(_6^{2-}\) anions enables the efficient packing of four C\(_2\)H\(_2\) molecules per unit cell and extraordinary C\(_2\)H\(_2\) uptake at 298 K and 1 bar.

In order to understand the exceptional C\(_2\)H\(_2\) adsorption in these materials, we conducted detailed first-principles DFT-D (dispersion-corrected density-functional theory) calculations. In SIFSIX-1-Cu, C\(_2\)H\(_2\) molecules are bound through strong C-H•••F hydrogen (H) bonding and van der Waals (vdW) interactions with the 4,4’-bipyridine linkers (Fig. 2). The DFT-D calculated static adsorption energy (\(\Delta E\)) is 44.6 kJ/mol. Each unit cell of SIFSIX-1-Cu contains four equivalent exposed F atoms and each exposed F atom binds one C\(_2\)H\(_2\) molecule. The distance between neighboring adsorbed C\(_2\)H\(_2\) is ideal for them to synergistically interact with each other through multiple H\(^{\delta+}\)•••C\(^{\delta-}\) dipole-dipole interactions, further enhancing the energy of adsorption. As four C\(_2\)H\(_2\) molecules are adsorbed per unit cell, the \(\Delta E\) of C\(_2\)H\(_2\) increases to 47.0 kJ/mol. The strong binding of C\(_2\)H\(_2\) at F atoms and the geometric arrangement of SiF\(_6^{2-}\) anions enables the efficient packing of four C\(_2\)H\(_2\) molecules per unit cell and extraordinary C\(_2\)H\(_2\) uptake at 298 K and 1 bar.

FIGURE 1: Schematic structure of SIFSIX-1-Cu. LEFT: The MOF building blocks. RIGHT: [001] and [100] views of the MOF crystal lattice. Color code: Cu, orange; Si, yellow; F, green; O, red; N, blue; C, gray; H: white.

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C₂H₂ adsorption is notably weaker in the wider pore material SIFSIX-2-Cu versus that in SIFSIX-1-Cu. The C-H-F H-bonding interaction from SiF₆²⁻ sites is of the same nature in these isoreticular networks (Fig. 2), while vDW interactions between C₂H₂ and the organic linker in SIFSIX-2-Cu is weaker compared to that in SIFSIX-1-Cu. However, in the twofold interpenetrated structure of SIFSIX-2-Cu-i, one C₂H₂ molecule can be simultaneously bound by two F atoms from different nets through cooperative C-H-F H-bonding, which enables the strongest energy of C₂H₂ binding (ΔE: 52.9 kJ/mol) yet observed in SIFSIX materials. The strong adsorption energy of SIFSIX-2-Cu-i contributes to its extremely high uptake capacity at low pressure.

The weakly basic SiF₆²⁻ sites and their geometric arrangement enable strong binding with weakly acidic C₂H₂ molecules. Because C₂H₂ is more acidic than C₂H₄ and the geometry is more optimal for C₂H₂ binding, there are much stronger interactions with C₂H₂ than C₂H₄ (ΔE in SIFSIX-1-Cu: 44.6 kJ/mol vs. 27.2 kJ/mol, SIFSIX-2-Cu-i: 52.9 kJ/mol vs. 39.8 kJ/mol). The calculated H-bond distances between C₂H₂ and SiF₆²⁻ sites are 2.541 Å and 2.186 Å in SIFSIX-1-Cu and SIFSIX-2-Cu-i, respectively, which are longer than those between C₂H₄ and SiF₆²⁻ sites.

To experimentally validate our DFT-D calculation results, high-resolution neutron powder diffraction data were collected on C₂D₂-loaded samples of SIFSIX-1-Cu⋅4C₂D₂ and SIFSIX-2-Cu-i⋅1.7C₂D₂ at 200 K to establish the structure of the C₂H₂ binding sites through Rietveld refinements. We found that each unit cell of SIFSIX-1-Cu is filled with four C₂D₂ molecules that are arranged in an ordered planar structure (Fig. 3), consistent with the DFT-D modeling results. C-D-F H-bonding occurs between C₂D₂ and SiF₆⁻ anions (2.063 Å), and D-F-C distances between neighboring C₂D₂ molecules are 3.063 Å and 3.128 Å. In SIFSIX-2-Cu-i, each C₂H₂ interacts with two SiF₆⁻ anions via dual C-D-F H-bonding (2.134 Å). These values are also in excellent agreement with our DFT-D predictions.

Next, transient breakthrough simulations were conducted on these materials in order to evaluate C₂H₂/C₂H₄ separation performances in column adsorption processes. Two C₂H₂/C₂H₄ mixtures (1/99 and 50/50) were used as feeds to mimic the industrial process conditions. Clean separations are realized with all five SIFSIX MOFs studied in this work. SIFSIX-2-Cu-i efficiently removes trace C₂H₂ from C₂H₄ gas (1/99) whereas SIFSIX-1-Cu demonstrates excellent C₂H₂ capacity with an uptake of 5533 mmol/L from 50/50 mixture. = 37 % greater than that of Fe-MOF-74. We further examined these materials in actual adsorption processes for both 1/99 and 50/50 mixtures through experimental breakthrough studies. Highly efficient separations for C₂H₂/C₂H₄ mixtures were indeed realized. For the capture of C₂H₂ from the 1/99 mixture, the concentration of C₂H₂ in the gas exiting the adsorber for up to 140 minutes was measured to be below 2 x 10⁻⁶ g/g and the purity of C₂H₄ was > 99.998 %, surpassing the industrial requirement (i.e., C₂H₂ below 5 x 10⁻⁶ g/g).

In summary, SIFSIX materials exhibit unprecedented C₂H₂ capture performance. We attribute it to the existence of sweet-spots in pore chemistry and pore size that enable highly specific recognition of C₂H₂ and high uptake to occur in the same material. Neutron diffraction combined with first-principles calculations have played a critical role in understanding the acetylene capture mechanism in these materials.

References
A novel route to achieving high thermoelectric performance in oxide materials

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Thermoelectric materials are capable of converting waste heat into useable electricity and have the potential to increase the efficiency of many technologies. These materials develop an electrical potential when subjected to a temperature gradient because of the Seebeck effect and conversely develop a thermal gradient when subjected to an electrical potential through the Peltier effect. Devices made from such thermoelectric materials are currently used for refrigeration and heating and are being widely explored for waste heat recovery [1]. To be effective, these materials must have low electrical resistivities to conduct the charge carriers with minimal loss, and a high Seebeck coefficient to produce sufficient voltages. Additionally, they should have minimal lattice thermal conductivity, because the thermal gradient must be maintained. These properties combine in a dimensionless thermoelectric figure of merit \( zT \), given by the formula \( zT = S^2T/\rho\kappa \) where \( S \) is the Seebeck coefficient, \( \rho \) the electrical resistivity, and \( \kappa \) the total thermal conductivity, measured at temperature \( T \). These properties are highly dependent, with metals possessing low electrical resistivities yet near zero Seebeck coefficients, and insulators with large Seebeck coefficients but prohibitively high electrical resisitivities. Finding new materials with optimal balances of these properties is key to understanding and improving thermoelectric efficiency.

Oxide materials possess many attractive qualities for use in high temperature waste heat recovery in air such as scavenging waste heat from car exhaust to improve vehicle fuel efficiency. They are preferred for such applications, as they are generally lightweight and air stable. Neutrons are crucial to structural studies of oxide thermoelectrics because the relatively low atomic number of the oxygen atoms makes X-ray characterization problematic. Oxide materials have not yet reached the level of performance of current state-of-the-art thermoelectrics, in part due to higher thermal conductivities compared to those of other material families, but additionally as a result of low power factors \( (S^2/\rho) \). While many oxides possess favorable Seebeck coefficients, finding oxides with the necessary metallic conductivities while retaining these high Seebeck coefficients has proven to be difficult [2]. Currently, the highest-performing oxide materials are \( p \)-type complex cobalt oxides that sprung from the discovery of high thermopower in metallic \( \text{NaCoO}_2 \) [3]. These compounds possess metallic resistivities yet retain high Seebeck coefficients. A key feature in all of the promising cobalt oxides are \( \text{CoO}_2 \) layers comprising mixed valent \( \text{Co}^{3+} \) and \( \text{Co}^{4+} \). The highly correlated, mixed valent cobalt ions provide the necessary electrical properties and the layered structure results in a low thermal conductivity, giving rise to a modestly high thermoelectric performance.

\( \text{PbPdO}_2 \), shown in Figure 1, is an attractive material for thermoelectric investigation because of the layered nature of the \( \text{Pd} \) square-planar units and heavy \( \text{Pb} \) atoms (suggesting potentially lower thermal conductivity) and the possibility for hole doping, which has been successful in other palladium oxide materials (suggesting control of electrical properties). In this study [4], we have prepared polycrystalline \( \text{PbPd}_{1-x}\text{Li}_x\text{O}_2 \) \( (0 \leq x \leq 0.08) \) in an effort to hole dope the material. Structural characterization was performed through neutron diffraction experiments collected on the BT-1 high resolution powder diffractometer and were coupled with electronic and thermal transport measurements to assess the thermoelectric performance.

Refinement of structural models against neutron diffraction patterns (Figure 2) was necessary not only because of the abundance of oxygen in the structure, but also to confirm the location and amount of \( \text{Li} \) substitution. Neutron diffraction

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revealed that for a nominal \( x = 0.08 \) sample, a Li content of \( x = 0.04 \) was achieved, and confirmed that it was substituted onto the Pd site in the material. This successful incorporation of Li had a dramatic effect on the electrical properties, shown in Figure 3. It was observed that even for the nominal \( x = 0.02 \) Li substitution, the material is metallic, as the resistivity dropped by an order of magnitude compared to that of stoichiometric PbPdO\(_2\). The resistivity decreases slightly further for the \( x = 0.04 \) sample, but remains roughly unchanged for higher substitution amounts, supporting the refined Li occupancy values from neutron diffraction. The Seebeck coefficient for the Li-substituted samples remains greater than 100 μV/K at room temperature. The Seebeck coefficient increases with temperature, approaching 200 μV/K at 600 K. The electrical resistivity and Seebeck coefficient of these Li-substituted materials is nearly identical to values reported for polycrystalline NaCoO\(_2\) [5]. The origins of the electrical properties in our materials differ from those of the cobalt oxides, suggesting alternate methods for achieving high thermoelectric performance in oxides.

In conclusion, we report the structural characterization and thermoelectric properties of Li-substituted PbPdO\(_2\). Neutron diffraction played an essential role in confirming the substitution amount and location of the Li dopant. Thermoelectric measurements indicate that our materials display similar electrical properties to those of some of the current high performing oxide thermoelectrics. Our findings suggest potentially new avenues to achieving high-performing oxide thermoelectric materials and encourage the search for such properties in oxides of metals more earth-abundant than the ones studied here.

References

Realization of ground-state artificial skyrmion lattices at room temperature

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Moore’s Law has been the icon of the computer revolution for nearly 50 years, but recent challenges with heat management and miniaturization have signaled its impending end. Spintronics – data and logic technologies that use the electron spin, in addition to the electron charge – offer a new approach to ultra-low power information technologies that may reinvigorate Moore’s Law. One promising spintronic technology is the magnetic skyrmion. Skyrmions are specialized configurations of magnetic moments into topologically-protected structures; a typical skyrmion structure, shown in Fig. 1, possesses a core and perimeter with opposite out-of-plane spin orientations, and a closed, continuous in-plane winding of magnetic moments between. These structures can be realized on the atomic scale, moved with very low electrical current densities, and are robust against moderate perturbations including stray fields and system defects. These make skyrmions very attractive for ultra-low power, high-density data storage and logic technologies. A key challenge to the development of skyrmion-based memory and logic devices is achieving skyrmion structures stable at ambient conditions (room temperature and no magnetic field).

Recently, we have realized ground-state magnetic skyrmions stable at ambient conditions by nanopatterning [1]. Specifically, cobalt nanodots with diameters of 560 nm and heights of 30 nm are patterned. The magnetic ‘vortex’ configuration within these dots, shown in Fig. 1 (red), form a closed winding structure, with an out-of-plane core, which is stable over a wide range of temperatures. However, a vortex lacks an out-of-plane perimeter, distinguishing it from a skyrmion. By placing a vortex-state nanodot on top of a magnetic film, the loop structure and core can be imprinted into the film. Thus, by designing a film with an out-of-plane orientation, the imprinted structure at the interface has a closed loop structure with an out-of-plane core and perimeter, e.g. a skyrmion. To prove this claim and demonstrate its viability for application, three pieces of evidence must be shown: (1) the direction of circulation of the loop structure, called the circularity, must be controllable, (2) the orientation of the core, called the polarity, relative to the perimeter must be controllable, and (3) the loop structure must, in-fact, be imprinted into the film underlayer.

Samples were prepared by a three-step process. In step one, multilayer films of [Co(0.5 nm)/Pd(1 nm)]10 were grown on naturally oxidized Si substrates; the multilayer structure gives the film a preferred out-of-plane orientation - called the perpendicular magnetic anisotropy (PMA). In the second step, hexagonal arrays of nano-holes with a diameter of 560 nm and center-to-center spacing of 1000 nm were patterned into a ≈ 400 nm thick polymer layer that was spin-coated onto the Co/Pd film. The holes are shaped like a circle, with one side made flat; the asymmetric structure has been previously used to realize circularity control. Next, the sample was irradiated by 1 keV Ar+ plasma, which suppresses the PMA in the regions exposed by the holes, while the regions still protected by polymer retain their PMA. During the third step, 32 nm of Co was deposited into the holes and the polymer mask removed, realizing asymmetric Co dots grown over the irradiated regions. Once the sample was fabricated, the skyrmion state was configured by a designed field sequence. First, the Co/Pd underlayer was saturated in the positive out-of-plane direction using a large out-of-plane magnetic field. Then, the out-of-plane field was removed and a small in-plane magnetic field was applied to saturate the dots parallel to the flat edge. At this point a small out-of-plane magnetic field was applied anti-parallel to the underlayer. The in-plane magnetic field was removed, nucelating a vortex, with the core biased to be anti-parallel to the underlayer. Lastly, the out-of-plane magnetic field was removed, leaving the system at remanence (no magnetic field) in a vortex state dot, with a core anti-parallel to the underlayer, and the region under the dot having no PMA.

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As stated above, circularity control was achieved by using the asymmetric dot structure. Applying an in-plane magnetic field parallel to the flat edge of the dot defines the nucleation site for the vortex and thus the circularity. Micrographs taken using scanning electron microscopy with polarization analysis (SEMPA) are shown in Fig. 2(a). The colors indicate the direction of the magnetization; the common color wheel for each of the dots indicates a common circularity of the magnetization. Other magnetic imaging technique and magnetometry measurements confirm the circularity control seen in SEMPA.

Recalling the magnetic field sequence to set the skyrmion state, polarity control is determined during the vortex nucleation by the small magnetic field applied anti-parallel to the underlayer. To demonstrate polarity control, the remanent magnetization was measured with the core parallel and anti-parallel to the underlayer. Specifically, the sample was prepared as discussed above, with the core anti-parallel to the underlayer and the out-of-plane magnetization measured as the magnetic field was decreased from remanence to negative saturation. In this case the magnetization of the core and perimeter are opposite, and thus subtract when measured together. Then, the sample was prepared again, but with the biasing field applied parallel to the underlayer. In contrast to the former case, the magnetization from the core and underlayer are expected to be parallel and add together. In a third measurement no biasing field was applied and the polarity was random. Indeed, as shown in Fig. 2(b), the skyrmion state, with the core and underlayer anti-parallel, has the smallest magnetization; the vortex state with the core and the underlayer oriented parallel has the largest magnetization; the random polarity falls in-between the parallel and anti-parallel configurations. This confirms the biasing field indeed defines the polarity.

Lastly, and arguably most crucially, the imprinting of the skyrmion was demonstrated using polarized neutron reflectometry (PNR), performed on the MAGIK reflectometer. PNR is a technique that uses scattering to extract depth-profiles from layered systems and possesses sensitivity to nuclear and magnetic features. The measured data are shown as dots in Fig. 3(a). A model was made to simulate the nominal structure and the reflectivity pattern calculated. By iteratively changing the model and comparing the calculated reflectivity to the data, the model converges on an accurate representation of the physical system. The converged model is shown in Fig. 3(b), and the corresponding reflectometry is shown as the solid lines in Fig. 3(a), which agree well with the experimental data ($\chi^2 < 1.2$). The converged model correctly identifies the designed structure, giving confidence in its accuracy. More importantly, the model identifies the magnetization of the Co dot - as expected - but also shows that the magnetization extends = 3 nm below the [Co/Pd]/Co-dot interface. This imprinted magnetic feature is the first direct evidence of the imprinted magnetic skyrmion. Further, the imprinted skyrmion is expected to be stable while the dots and underlayer are stable (ambient conditions up-to approximately 300 °C, and 300 mT). Theoretical modeling using NIST’s object oriented micromagnetic framework (OOMMF) confirms that the imprinted structure extends 2 nm into the underlayer.

In summary, we have successfully achieved room temperature artificial skyrmion lattices in the ground state over extended areas, defining a platform for exploring skyrmion properties and behaviors as well as the use of skyrmion lattices in novel technological concepts. The system is constructed by fabricating circularity controlled Co nanodots on a selectively irradiated Co/Pd underlayer with PMA. Circularity control is imposed by the fabrication of asymmetric dots and confirmed by microscopy. Polarity control is realized by the application of a small out-of-plane magnetic field during the vortex nucleation, and demonstrated in the magnetization curves. The imprinted skyrmion lattice in the Co/Pd is directly confirmed by PNR, and is quantitatively consistent with micromagnetic simulations. These artificially constructed skyrmion lattices are stable over a wide range of magnetic fields and temperatures, including room temperature and zero magnetic field. These foundational results present a new path in skyrmion research on the meso-scale, at and above room temperature.

Reference

Magnetic order, electronic structure, and electrical transport are strongly intertwined in correlated materials. The symmetries of a particular correlated state dictate different classes of charge transport phenomena that may be observed. For example, in a material that has ferromagnetic order where time-reversal symmetry is broken, electrons acquire a velocity transverse to electric current and magnetization. This effect (known as the anomalous Hall effect) originates from both spin-dependent scattering and intrinsic quantum mechanical properties of the electronic wave function (Berry curvature) of the filled bands. The latter contribution becomes significant if the electronic band structure has band-crossing points that develop energy gaps with the breaking of time-reversal symmetry. In the fully quantum limit in two dimensions (2D) where the Fermi level is located within such a gapped region, the anomalous Hall conductivity is quantized in units of $e^2/h$, where $e$ is electron charge and $h$ is Planck’s constant, which has been observed experimentally in the ferromagnetic topological insulator Cr$_x$(Bi,Sb)$_2$Te$_3$ [1].

More complex ordered materials such as antiferromagnets can also exhibit the anomalous Hall effect; this is most commonly seen when the constituent spins have a non-coplanar ordering pattern with finite net scalar spin chirality $\chi_{ijk} = \vec{S}_i \cdot (\vec{S}_j \times \vec{S}_k)$, where $\vec{S}_i$ are spins [2]. In addition, if the spins have an ordering pattern that breaks the combined time-reversal and lattice symmetry of the material, the Berry curvature of the filled bands can contribute to the anomalous Hall effect as in ferromagnets [3]. This last phenomenon has been recently explored in materials with a kagome network, but its applicability to a general class of materials is an open question.

Recently, we found that the antiferromagnet GdPtBi shows a large anomalous Hall conductivity and used elastic neutron scattering and electronic structure calculations to confirm it belongs to this newest class of effects [4]. GdPtBi has a half-Heusler structure composed of a face centered cubic Gd sublattice responsible for magnetism of the system and a nonmagnetic zinc blende PtBi sublattice (Fig. 1). Theoretical calculations have revealed that the electronic band structure near the Fermi level is mainly determined by the PtBi sublattice and has band touching around the Fermi level similar to that of the topologically non-trivial material HgTe. A critical difference between HgTe and GdPtBi is the existence of localized magnetic moments, which affect the electronic structure via magnetic ordering. It is known that this compound exhibits antiferromagnetic ordering below $T_N = 9$ K, where the Gd moments order ferromagnetically in the (111) plane and are coupled antiferromagnetically along the [111] direction (called type-II ordering) in zero magnetic field, as shown in Fig. 1(b) [5]. From the Curie-Weiss fitting of the high temperature magnetization data, the Weiss temperature $Q_{CW}$ $\approx 38$ K. This gives a moderate frustration parameter $f = \theta_{CW}/T_N = 4$, implying that there are other magnetically ordered states with comparable energy. It has been proposed theoretically for the face centered cubic structure that such a spin system may exhibit an anomalous Hall effect originating from scalar spin chirality $\chi_{ijk}$ if the spins order in a multiple-$q$ spin structure with $q \parallel <001>$ [6]. To elucidate whether the observed anomalous Hall effect originates from the scalar spin chirality or the Berry curvature mechanisms, the magnetic structure in finite field needs to be determined experimentally.

We have performed elastic neutron scattering measurements using $^{160}$Gd-enriched GdPtBi single crystals on the triple-axis spectrometer BT-7 at the NIST Center for Neutron Research. Figure 2(a) shows the temperature dependence of the (0.5 0.5 0.5) magnetic Bragg peak intensity in zero magnetic field. This peak

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**FIGURE 1:** (a) Crystal structure of GdPtBi, which is composed of (b) a magnetic Gd face centered cubic sublattice and (c) a PtBi zinc-blende sublattice. Red arrows in (b) show the type-II antiferromagnetic ordering pattern.
is allowed in the presence of type-II antiferromagnetic ordering. The intensity increases with decreasing temperature below $T_N = 9\,K$ as expected. The evolution of the magnetic Bragg peak (0.5 0.5 2.5) from the type-II ordering with applied magnetic field is shown in Fig. 2(b). The intensity increases up to $6\,T$ and shows saturation above that field. This tendency is seen more clearly in the integrated Gaussian area obtained by fitting the profile to a single Gaussian function, as shown in Fig. 2(e). We have performed the measurements at all half-integer (HHL) with $Q < 3.7\,\text{Å}^{-1}$ and observed the same trend. Figure 2(c) shows the profile of the (111) peak originating from the nuclear Bragg scattering as well as the magnetic one from the ferromagnetic component of the spin ordering, whose intensities are additive. The magnetic intensity increases with increasing magnetic field and the increase of the integrated Gaussian area scales with the square of the magnetization (Fig. 2(e)). We have also examined the possibility of the multiple-$q$ spin structure with $q || <001>$, but no evidence for the presence of such a structure was obtained, as shown in Fig. 2(d).

The spin structure deduced from the obtained results is shown in Figs. 2(f) and 2(g). The spins align antiferromagnetically in zero field and cant toward the magnetic field direction in finite field. As the canting represents a ferromagnetically ordered component in the spin structure, the symmetry requirement for finite anomalous Hall effect (that the combined time-reversal and lattice symmetry should be broken) is fulfilled. Furthermore, spin-dependent electronic band calculations based on the magnetic structure revealed that the band crossing point existing in the collinearly ordered state is lifted along the high symmetry direction and Weyl points possibly appear by spin canting caused by applied magnetic field. Both features in the electronic structure may contribute to the Berry curvature and the resulting large anomalous Hall effect. This mechanism that has been extensively investigated in ferromagnetic system is therefore now a new target for study in antiferromagnets which host a rich variety of complex orders. The current study extends the generality of the mechanism to the half-Heusler antiferromagnet and demonstrates the ubiquity of the role of Berry phase in symmetry-broken system.

**References**

Beyond the interface limit: structural and magnetic depth profiles of voltage-controlled magneto-ionic heterostructures

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Oxidation is a common process that changes virtually every quality of a material, including optical, mechanical, electrical, thermal, and magnetic properties. For example, metals are typically shiny, ductile, conductive, and can be magnetic, while metal oxides can be matte or transparent, brittle, insulating, and are frequently non-magnetic. Controlling oxidation by electric fields offers an opportunity for manipulating the material properties with the flip of a switch. This is the premise behind both memristors, which use a voltage to control oxygen distributions and tune electrical conductivity, and magneto-ionic devices [1-5], which similarly use a voltage to tune magnetic properties. These technologies work by recognizing that metal oxides are ionic solids with oxygen atoms that have a net charge and thus are sensitive to electric fields. Applying a strong electric field can thus alter the oxygen ion distribution, changing the material properties. Recent investigations [1, 2] have demonstrated magneto-ionic control in ultra-thin Hall bar structures (thicknesses < 1 nm). In these studies, the films prefer to have the magnetization oriented out of the plane of the film; using an electric field to drive oxygen into the interface with a neighboring oxide material causes the magnetization to rotate into the plane of the film. Devices built on this control have been proposed for ultra-high density, low-power data storage technologies. However, for broader applications, ion-based control must be demonstrated in thicker films with bulk-like properties, and it is unclear how the magneto-ionic control mechanism works in this regime.

In this work, we demonstrated magneto-ionic effects in comparably thick (15 nm) cobalt films [5]. Using an applied voltage, oxygen was driven from a GdOx/AlOx film into the neighboring Co film, which then becomes non-ferromagnetic CoOx. Magnetometry revealed that, while some of the magnetic properties are recovered, others are not. Using polarized neutron reflectometry (PNR), the depth-resolved oxygen distribution and magnetization were directly mapped, providing a physical picture to explain the observed behavior.

Thin-films with a structure Si/Pd(50 nm)/AlOx(1000 nm)/GdOx(2 nm)/Co(15 nm)/Pd(20 nm) were grown by sputtering and e-beam evaporation at the Center for Nanoscale Science and Technology. Electro-thermal (E+T) conditioning was performed by heating the sample to 230 °C and applying 40 V across the Pd layers for 15 min. The measured PNR reflection and spin-asymmetry (SA) for the as-grown sample, the sample after applying + 40 V (anode on the top surface), and sequential - 40 V are shown in Figs. 1(a) and (b), respectively. The SA, which is proportional to the product of the magnetization and nuclear scattering length density (SLD), is shown to decrease after the + 40 V treatment and partly recover after subsequently applying - 40 V. Using the Refl1d software package, models for the three treatments (as-grown, after + 40 V, and after sequential +/- 40 V) were fitted in parallel, Fig. 1(c). The fitted model for the as-grown sample closely matches the designed structure and the bulk nuclear SLD for these materials, lending confidence to its accuracy. After the initial + 40 V treatment the nuclear SLD increases in the Co layer, the GdOx/Co interface becomes much broader, and the

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magnetic SLD decreases (38%), most prominently at the interface (80%). This is consistent with oxygen being moved by the electric field from the GdO\(_2\) layer into the Co layer, forming non-magnetic CoO. Subsequently applying - 40 V restored the sharp nuclear interface and most of the magnetism (92%). However, oxygen migration was irreversible for thicknesses greater than 10 nm. Measurements performed using a thermal-only treatment showed a much smaller effect, demonstrating that the electric field moves oxygen into and out of the Co layer depending on its polarity.

Magnetic first order reversal curve (FORC) measurements of the as-grown sample, the +/- 40 V sample, and a thermally treated sample (230 °C for 30 minutes) are shown in Fig. 2. The FORC plots, in a general sense, are a map of all hysteretic events that exist within a system and provide detailed information regarding the magnetic reversal process. The FORC distribution for the as-grown sample shows only a single feature, indicating a single magnetic phase. By comparison the electro-thermal and thermal-only samples show two features, with a new feature located at \(H_C = 0\) that specifically identifies reversible features. In general, reversible features indicate the absence of hysteresis and are often manifest when the magnetism is measured along a hard axis. We suggest that the new reversible phase is the result of a decoupling between grains within the Co film plane. Specifically, the film is comprised of many nano-scale magnetic grains, each with their own randomly oriented magnetocrystalline anisotropy. Typically, magnetic exchange coupling between neighboring grains can cause the film to behave as a single coherent structure. The small amount of residual oxygen may be interrupting the exchange interaction, allowing the magnetocrystalline anisotropy of each grain to dictate its orientation.

We suggest the reduced exchange interaction and irreversibility for thicknesses of > 10 nm is due to a screening effect of the electric field, as shown in Fig. 3. Specifically, the + 40 V electro-thermal treatment moved oxygen deep into the film, diffusing quickly at grain surfaces and more slowly in the bulk. During the - 40 V treatment the oxygen migrated quickly off of the grain surface, leaving a metallic Co shell. This shell screens the electric field via the Faraday effect, thus halting any further migration and trapping oxygen within each grain and deeper in the film. This mechanism suggests an unexplored role of the microstructure, and a potential limit to these technologies.

In summary, we have realized a thin film magneto-ionic device built on a thick (15 nm) Co film. Semi-reversible control of the magnetism resulting from oxygen migration was demonstrated and directly mapped using polarized neutron reflectometry. First order reversal curve measurements showed that the nominally similar sample possessed two phases, while the as-grown sample had only one. Based on a fundamental understanding of the nature of electric fields and oxygen migration, a physical picture was presented which supports the results. This work thus demonstrates that ionic devices with ‘active’ layers thicker than a few atom layers are still viable, thus opening new opportunities for future ion-based technologies.

References


Solar cells based on the hybrid halide perovskite CH$_3$NH$_3$PbI$_3$ have achieved efficiencies as high as 20%. Despite tremendous work on these systems [1], it is still not clear what role the CH$_3$NH$_3^+$ (methylammonium, MA) cations play in enhancing solar cell performance. For instance, while the most stable form of MAPbI$_3$ is non-polar, it has been suggested that the organic cation dipoles may also orient into ferroelectric domains, which affect the electronic band structure and slow carrier recombination. The ability to probe local dipole dynamics and ferroelectricity would greatly improve our understanding and assessment of this hypothesis. To shed some light on the influence of the MA cations, we present a combined neutron scattering and first-principles computation study of the structure and dynamics of MAPbI$_3$ [2].

The temperature-dependent powder diffraction data from MAPbI$_3$ show two phase transitions (Fig. 1). For $T > 300$ K to $335$ K, the structure is cubic with space group P4mm. The system changes to a tetragonal phase with symmetry I4cm below $300$ K, and with further cooling below $160$ K transforms to an orthorhombic phase with space group Pnma. The lattice parameters, bond angles, and atomic positions were determined by full structural Rietveld refinement [2]; the refinement and difference plots indicate a very good fit to the powder diffraction data (Fig. 2). Focusing on the low-temperature orthorhombic phase, each unit cell contains four symmetry-related CH$_3$NH$_3^+$ molecules with C-N bonds confined to the ac-plane (see insets to Fig. 1 and Fig. 2). The molecules at sites 1-4 (inset to Fig. 2) have orientations L (C to the left of N in the c-axis projection) or R (C to the right of N). The non-polar ground state is labeled LLRR. We also examined three other symmetry-distinct orientations of the four dipole moments in the unit cell, i.e., RRRR, LRRL, and LRRR. First-principles computations show that the energy difference between the non-polar LLRR phase and the other possible ferroelectric phases is quite small, on the order of a few meV per atom, and the barrier between them is around 0.3 eV. Hence local dipole dynamics should be present, and less commonly, ferroelectric domains may form.

The observed inelastic neutron scattering (INS) spectrum is shown in Figure 3 in comparison to computed one- and two-phonon spectra for the non-polar (LLRR) orientation. The agreement between the measured data and calculations is good; in particular, we notice significant multi-phonon scattering in the observed spectrum. The phonons below 25 meV are mainly PbI$_3$ sub-lattice phonons, while those above 25 meV are the vibrational modes of the MA cations. Diagonalizing the dynamical matrix with and without the off-diagonal coupling terms, we find that there is strong coupling between the low-energy PbI$_3$ modes and MA rotational modes. The CH$_3$NH$_3^+$ ion thus controls the final structure and dynamics due to its strong hydrogen bonding and steric (i.e. space filling) effects, even while it is decoupled electronically from the PbI$_3$ bands. The lowest energy vibrational mode of the MA is found to be around 39 meV, corresponding to the twisting of CH$_3$—NH$_3$ groups around the C-N bond. Near 100 meV, another significant high-energy mode corresponds to the bending of the CH$_3$—CH bond/CH$_2$—NH$_3$ bond angles.

Figure 4 shows the calculated INS spectra for the symmetry-distinct cation orientations and the overall dipole moment of each system. These results demonstrate that the lattice

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dynamics are sensitive to the local ordering of the MA dipoles in the structure. In the cases of RRRR and LRRR, there are two and four non-equivalent MA ions in the cell, respectively, and therefore the CH$_3$/NH$_3$ twisting mode energies are split. There are also significant changes to the low-energy modes of the PbI$_3$ sub-lattice due to strong CH$_3$NH$_3$-PbI$_3$ interactions. Hence we propose measuring the CH$_3$/NH$_3$ twisting mode energies to obtain a local probe of the local dipole moment orientations.

In conclusion, we have revealed the role of organic CH$_3$NH$_3^+$ ions in determining the structural and dynamical properties of the hybrid halide perovskites. Even though CH$_3$NH$_3^+$ is disconnected electronically from the band structure of the PbI$_3$ sub-lattice, it controls the PbI$_3$ network geometry due to structural interactions and space filling effects. The ground state is non-polar, but ferroelectric states where the dipole moments are ordered in parallel are very close in energy, with small barriers of ≈ 0.3 eV. The spontaneous dipole moment is dominated by the off-centering of the MA ions with respect to the PbI$_3$ framework rather than due to dipole moment of the MA ions itself. We find that the CH$_3$/NH$_3$ twisting mode energy is especially sensitive to the ordering of the CH$_3$NH$_3^+$ ions with dipole moments, and that it shifts and splits significantly depending on the surrounding MA orientations. We therefore propose using the vibrational dynamics of MA ions as a local probe of the dipole ordering. Under an electric field, one may stabilize different ferroelectric domains that can be monitored via the vibrational spectrum of MA. Such ferroelectric ordering, and its impact on the performance of the hybrid halide perovskite solar cells, could then be accurately quantified and understood.

References


Magnetism in a solid typically arises as a consequence of the orbital state of unpaired electrons and the cooperative alignment of these spin and orbital magnetic moments. In contrast to this conventional magnetic order, ordered patterns of orbitals themselves can play an important role, particularly in f-electron materials, and create exotic new types of phases where novel properties emerge [1]. Though quite interesting, these new types of multipole orbital orders are difficult to probe because common techniques to elucidate the thermodynamic order parameter, such as neutron Bragg scattering or Mossbauer spectroscopy, couple directly only to the dipole moments and not the higher-order moments. Hence these new types of order are often referred to as “hidden order”, and have attracted a great deal of attention. One prototype class of materials where hidden order emerges is on the magnetically frustrated cubic pyrochlore lattice, such as $\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y}$, which is the system of present focus. We have investigated this system employing diffraction and inelastic neutron scattering, specific heat, magnetization, and Monte Carlo calculations, and have succeeded in demonstrating that the ordered state originates from electric quadrupole moments intrinsic to the $\text{Tb}^{3+}$ ions [2]. This is the first example of electric quadrupole order in a frustrated magnetic system, and opens new research directions for “frustrated quadrupole systems”.

The magnetic ground state of $\text{Tb}_{2}\text{TiO}_{7}$ (TTO) does not exhibit either the usual long range magnetic order, or a (frozen) spin glass, but rather exhibits fluctuating moments down to very low temperature (viz. 0.07 K) [3]. The pyrochlore structure consists of a corner-sharing network of tetrahedra that exhibit prototypical geometrical frustration [Fig. 1(a)]. A classical treatment of the magnetic system indicates that TTO should undergo a transition to magnetic (dipole) long range order (LRO) at about 1 K, and thus is considered a candidate quantum spin liquid (QSL). However, despite many theoretical and experimental studies, the actual nature of the ground state has remained elusive, partly owing to a sample dependence of the properties that depend very sensitively on the precise stoichiometry of the system. For example, it was found that some crystals showed a clear specific-heat peak at $T = 0.4 \text{ K}$ suggesting a phase transition, but without magnetic LRO. Indeed recent studies on polycrystalline samples revealed a dramatic sensitivity to the $x$-value of $\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y}$, where a mysterious order appears in the vicinity of the QSL state ($x > -0.0025 = \chi$), although the origin of the QSL and its relation to the order were not clear.

Therefore it is essential to be able to fine-tune the composition of high quality single crystals, and we have recently succeeded in this synthesis. This has enabled the elucidation of the key ingredients of the hidden order using a crystal with $x = 0.005$ ($T_C = 0.53 \text{ K}$). Figure 1(b) shows the $T$ dependence of specific heat under an applied magnetic field along the [111] direction, up to 1 T. Since the [111] direction is one of the characteristic directions of the pyrochlore lattice [Fig. 1(a)], it should be a good direction to observe typical behavior of the ordered state. Indeed, the sharp peak at $T_C$ survives only up to 0.1 T, turning into broad double

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peaks at 0.3 T. The $H$ dependence of the higher peak ($T_C$) exhibits a similar behavior for the $H$ dependence of the peak of systems showing a hidden or multipole order [inset of Fig. 1(b), Fig. 2(a)]. It is also found that the spectrum of inelastic neutron scattering and magnetization both show abrupt changes in accordance with the ordered state.

An interesting theoretical scenario has been recently proposed by Onoda and Tanaka to understand this behavior [4]. They consider a pseudospin-1/2 Hamiltonian for pyrochlore systems with non-Kramers ions such as Tb$^{3+}$ (or Pr$^{3+}$), and show that transverse super-exchange interactions between quadrupole moments, which are set into the spin ice Hamiltonian as an additional term, play the driving force of the order, transforming it into a type of a quadrupole order in the vicinity of a SL state. We therefore analyzed the experimental data based on this model, and found that the data can be reproduced by parameters in an electric quadrupole phase located very close to the phase boundary between the quadrupolar and U(1) QSL states [Fig. 2(b)]. This result also agrees with the interpretation of the previous experimental result that the minute change of $x$ of Tb$_{29}$T$_{1}$O$_{7+y}$ brings about the change in states between QSL and LRO. These results indicate that the problem of the hidden order in TTO can now be reconsidered as the novel problem of quadrupole order on the frustrated pyrochlore lattice with the non-Kramers ion of Tb$^{3+}$. These results also suggest that the putative SL state of TTO studied for more than decade could be the U(1) QSL.

All the above comparisons between the experiments and theories reveal that the low temperature ordered state of TTO is quadrupole in nature. Although neutrons do not couple directly to the primary order parameter for this type of order, important clues to the order are nevertheless evident. In particular, weak reflections develop at the forbidden (002) position and at the superlattice type (1/2 1/2 3/2) position [Fig. 3], and polarized neutron data on BT7 reveal that both of them are magnetic. The long-range ordered magnetic moments of these reflections are only $0.1 \mu_B$, too small to be the primary order parameter. It appears that the (002) reflection develops simultaneously with the quadrupole order, with an order parameter characterized by the wave vector $k = 0$ that is induced by higher order terms neglected in the theoretical model. On the other hand, the (1/2 1/2 3/2) reflection (also observed in a powder sample) exhibits a different $T$ dependence, suggesting it has a different physical origin. Since electric quadrupolar orders are related to the deformation of $f$-electron charge density, these naturally couple to displacements of ligand ions and may induce cooperative Jahn-Teller (JT) effects, providing new pathways to investigate these multipole order parameters. Moreover, the model parameters suggest that this composition of TTO is very close to the putative spin-liquid state. Investigations in the context of a Higgs transition, and following the evolution of the system to the nearby U(1) quantum spin liquid state are fascinating future directions to explore.

References

Pairing of electrons into Cooper pairs in conventional superconductivity is mediated by phonons. In unconventional superconductors including cuprates, iron pnictides, and heavy fermion superconductors such as CeCoIn$_5$, the ‘pairing glue’ is likely to be magnetic fluctuations. In the superconducting state of these unconventional superconductors, a prominent magnetic resonant mode appears at the antiferromagnetic wave vector at energies that roughly scale with the superconducting transition temperatures ($T_c$). The magnetic resonance mode is a ‘common thread’ for unconventional superconductors [1] and revealing its nature is a prerequisite for understanding the mechanism of superconductivity mediated by spin fluctuations.

The magnetic resonance mode is commonly interpreted as a spin-exciton [2], although it has also been proposed to be a remnant magnon-like mode revealed due to reduction of damping in the superconducting state. In the spin-exciton picture, the magnetic resonance mode can be calculated from structures of the Fermi surface and the superconducting order parameter. For cuprates with d-wave pairing symmetry, the magnetic resonance mode exhibits a prominent downward dispersion while in iron pnictides with s-wave pairing symmetry the mode displays an upward dispersion. In both cases experimentally measured dispersion agrees with what is expected in the spin-exciton picture.

Superconductivity in CeCoIn$_5$ ($T_c = 2.3$ K) has d-wave pairing symmetry similar to the cuprates, and the resonance is expected to display a downward dispersion as in the cuprates. Our results on MACS instead clearly demonstrate a prominent upward dispersion, as shown by constant-energy slices of magnetic scattering at several energy transfers in Figure 1. With increasing energy transfer from $E = 0.5$ meV in Figure 1 (a) to 1.0 meV in Figure 1 (d), the magnetic resonance mode disperses out, exhibiting a ring-like features at $E = 1.0$ meV. The dispersive feature is only observed in the superconducting state, whereas in the normal state ($T > T_c$) magnetic excitations are centered at $Q = (0.5, 0.5, 0.5)$ for all measured energies.

It has been shown that the electronic structure of CeCoIn$_5$ is significantly modified by Yb doping. If the magnetic resonance mode is a spin-exciton which results from the Fermi surface and the superconducting gap structure, then it should be strongly affected if the Fermi surface or the superconducting gap structure is modified dramatically. Our results on MACS reveal that the dispersion of the magnetic resonance mode remains robust with Yb doping, although considerably broadened, as shown in Fig. 2. For both Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ ($T_c = 2.25$ K) and Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$ ($T_c = 1.5$ K) the magnetic resonance modes exhibit clear upward dispersions, as shown in Fig. 2 (a) – (d). More strikingly, the dispersion hardly changes compared to CeCoIn$_5$, as shown in Fig. 2 (e) – (g). Therefore, despite the changes of electronic structure with Yb doping, the dispersion of the resonance remains robust.

**FIGURE 1:** Constant-energy maps of inelastic neutron scattering cross sections for CeCoIn$_5$ measured on MACS cold neutron spectrometer for several energies transfers. (a) $E = 0.5$ meV, (b) $E = 0.6$ meV, (c) $E = 0.8$ meV and (d) $E = 1.0$ meV. The data at $T = 0.1$ K ($T < T_c$) after subtracting the data at $T = 2.5$ K ($T > T_c$) is shown; all observed features correspond to the magnetic resonance mode.
The observation of a prominent upward rather than downward dispersion of the magnetic resonance mode and insensitivity of the dispersion to changes in electronic structure both challenge the view of the mode being a spin-exciton. Our results suggest that the mode could be magnon-like excitations and the robust dispersion reflects a robust effective nearest neighbor exchange coupling in this system, although our observation can be due to either itinerant or local magnetism. This idea is in agreement with the fact the magnetic resonance mode in Ce$_{1-x}$Yb$_x$CoIn$_5$ display strong $L$-modulation, as can be seen in Fig. 1 and Fig. 2, in contrast to the cases of cuprates and iron pnictides where the mode form rods along $L$. In addition, as shown in Fig. 3 the dispersion of the magnetic resonance mode in Ce$_{1-x}$Yb$_x$CoIn$_5$ resembles the dispersion of spin waves in antiferromagnetically ordered CeRhIn$_5$, although with a slightly reduced dispersion velocity. The reduced dispersion velocity in Ce$_{1-x}$Yb$_x$CoIn$_5$ compared to CeRhIn$_5$ is reminiscent of similar results in cuprates where upon doping the dispersion of magnetic excitations is found to soften.

In summary, using MACS we have established a robust upward dispersion for the magnetic resonance mode in Ce$_{1-x}$Yb$_x$CoIn$_5$. Our observation challenges the common view that the magnetic resonance mode in CeCoIn$_5$ is a spin-exciton, and suggests the presence of magnon-like excitations being a common feature of unconventional superconductors.

References

In 2009 President Obama proposed a new national fuel program that mandates a gradual rise in fuel economy to an average mileage (cars and light trucks) of 54.5 mpg by 2025. This goal is about 50 % higher than the 2016 mandate posing a serious challenge to the automotive industry. Industries are pursuing two major themes to achieve this ambitious goal: (1) more efficient engine technologies with hybrids and plug-in electrics, and (2) broad spectrum efforts to reduce vehicle weight. Automotive lightweighting requires the use of new materials that combine two properties: elongation to large strains and high strength. The first describes the capacity to stretch during forming or under crash conditions while the second (strength) is crucial to allow thinner gages that bring weight reduction. While these materials have been developed, wide adoption in car body parts has been slowed by a severe lack of data regarding their deformation behavior. Such knowledge is essential because the stresses necessary to strain a metal sheet into a part with a precisely defined shape must also be known precisely.

The measurement of plastic stress-strain properties ($\sigma(\varepsilon)$ laws) is straightforward in uniaxial deformation but very difficult in two dimensions with additional complications in path changes, e.g. sequences of straining in different directions. The reason for this difficulty is evident in Figure 1 through the highly inhomogeneous distribution of shear strains. The sub-millimeter spatial resolution of the strain field is made possible through in-situ digital image correlation (DIC). Neutron diffraction is the complement to the strain from DIC – a neutron beam is focused on the center of the sample in the near-homogenous strain region, and the elastic lattice strains measured by diffraction provide the stress tensor. This experiment is enabled by a novel straining device specifically built for neutron diffraction with in-situ DIC [1]. Here, shear is achieved by mutually perpendicular compressive and tensile stresses of equal magnitude. The relative standard deviation $\sigma_{rel}$ of strains in the entire sample is almost eight times larger than in the beam-exposed center ($\sigma_{rel}^{beam} = 0.05$), which precludes the use of averaging force sensor data.

The combination of DIC and neutron diffraction stress analysis can provide new insights into the shear test as commonly used in sheet metal testing. Specifically, a large difference between the local $\sigma_{xy}(\varepsilon_{xy})$ law (subscript $xy$ = shear) and the average is revealed with the largest spread found between load cell based stresses of two very similar samples as shown in Figure 2. This difference hints at a considerable effect of the specimen geometry on the average stress obtained from the load cell.

The stresses measured by neutron diffraction on the other hand are very similar – as they should be for samples of the same material. The implication is that neutron diffraction provides data with better accuracy for an important sheet metal forming test, and the consequences extend beyond the monotonic $\sigma_{xy}(\varepsilon_{xy})$ curves. While the forming of an automotive body part involves shear it rarely does so in pure form with the exception of deep drawing such as beverage cans. Monotonic $\sigma_{xy}(\varepsilon_{xy})$ curves are therefore just one piece of the puzzle of large strain deformation. However, sequences of tensile stretching and compressive shortening are common in forming, and that is where the shear test finds another use. Reversals between forward and backward shear are very easy to perform even at large strains and without buckling which restricts the utility of uniaxial load reversal tests (the problem of compressive buckling was first investigated by Leonard Euler more than 250 years ago). The effects of reverse deformation after some plastic strain has already been accumulated (the pre-strain) can be described as a yield drop, i.e. the magnitude of stress necessary to initiate...
plastic deformation in the opposite direction is lower. This observation is known as the Bauschinger effect. Its importance lies in the fact that the magnitude of the yield drop depends, among other factors, on the pre-strain as shown in Figure 3. The basic mechanism responsible can be understood though the concept of back stress created by dislocation networks that are arranged in stable cells within grains. The back stresses, sometimes called long range internal stresses (LRIS), increase with plastic strain and they act against the external applied stress – if the applied stress is reversed the back stresses now aid the movement of free dislocations, hence the stress necessary to produce reverse strain is now lower. The inset in Figure 3 describes the yield stress before and after load reversal. The yield drop is the difference between the (absolute) yield stress in forward shear and immediately after reversal of shear. The yield stress in forward shear (inset, red graph) can be described by a power law type behavior ($\sigma_{\text{yield}} = A\varepsilon^n$ with $200 < A$ (MPa) $< 400$ and $0.1 < n < 0.4$, depending on whether deformation occurs in forward or reverse shear). It should be noted that the hardening coefficient $n$ is smaller in reversal. This is another consequence of the Bauschinger effect, and it is called work hardening stagnation expressed by the lower increase in stress after reversal. The law describing the yield stress after reversal (purple graph in the inset) appears to be nearly linear suggesting that the yield drop becomes smaller at even larger strains $> 0.22$; however, it is unlikely to continue in this manner at larger pre-strains; rather, a similar plateau for the reverse yield stress can be expected, most likely leading to a plateau in the yield drop for strains $> 0.2$.

The observations made here regarding the effects of pre-strain and load reversal are not new in qualitative terms; however, the magnitudes of stress and strain have been put on a much sounder footing though the simultaneous use of digital image correlation strain measurement and neutron diffraction stress determination. Both methods offer spatial resolution as a remedy to the inherent inhomogeneity of stress and strain fields in multiaxial testing.

Reference

Precision measurement of the radiative beta-decay of the free neutron

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In the six decades since the first measurement of the neutron lifetime, the study of neutron beta decay has provided increasingly precise tests of the Standard Model and important input to cosmology and other areas of physics [1]. Precision measurements of neutron observables, such as the lifetime and the spin-electron asymmetry coefficient, currently allow for comparisons with theory with a precision below 1 %. The Standard Model predicts that the decay of the free neutron can produce one or more detectable radiative photons in addition to a proton, an electron, and an antineutrino. Here we summarize the results of the RDK II experiment [2], which includes the first precision test of the shape of the photon energy spectrum and a substantially improved determination of the branching ratio. This demonstrates that measurements of the neutron’s radiative decay mode can probe new physics. A measurement of the photons’ circular polarization could reveal information about the Dirac structure of the weak current [3, 4], and a possible source of time-reversal violation would be apparent in a triple-product correlation between the antineutrino, electron, and photon [5]. Increased precision would allow a test of a heavy baryon chiral perturbation theory calculation [4].

In contrast with the long history of most neutron beta-decay measurements, experimental studies of neutron radiative beta decay are relatively recent [6]. In 2006 the RDK I collaboration reported the first definitive observation of radiative decay. The RDK II experiment improved upon its predecessor by reducing statistical uncertainties through the use of additional photon detectors, improving the understanding of systematic uncertainties through detailed energy response studies of the detectors, and significantly extending the detectable photon energy range to between 0.4 keV and the 782 keV photon energy endpoint. Radiative photons from neutron decay originate from either electron, proton, or vertex bremsstrahlung. Electron bremsstrahlung dominates while higher order terms contribute less than 1 % to the branching ratio [4].

The RDK II experiment operated at the NG-6 fundamental physics end-station at the NCNR for one year, with a typical neutron fluence rate of $1.1 \times 10^8$ s$^{-1}$. The cold neutron beam was guided to the active region defined by the fields (dashed lines) created by the solenoids (gold) and the electrostatic mirror (blue). Protons and electrons follow the field lines to the SBD (light blue). Radiative photons were detected by twelve bismuth germanate (BGO) crystals (green) and three large area avalanche photodiodes (APDs). The detection probability in independent arbitrary units (A.U.) for electron-proton (ep) and electron-proton-photon (epγ) detection coincidence for either the BGO or direct APD detectors. This plot is approximately aligned with the diagram above.

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Neutrons which decayed between the mirror and the bend produced electrons and protons capable of being detected by the apparatus. The electrons and protons followed adiabatic helical orbits about the field lines with maximum cyclotron radii of approximately 1 mm. Electrons emitted in the downstream direction typically escaped the electrostatic mirror. Electrons emitted in the upstream direction typically hundreds of keV each, were likely sufficient to overcome the magnetic field, which would allow for particle tracking and improved detection-volume definition. In addition, photon detectors with better proportionality could be implemented, and improvements in low-energy proton detection would allow better identification of proton and electron events. Utilizing a higher intensity cold neutron source should significantly improve the ability to study systematics while maintaining high statistical precision.

The final data set consisted of 22 million electron-proton (ep) detections, for which about 20,000 and 800 radiative photons were detected in coincidence (epγ) with the BGO and APD detectors, respectively. The dominant systematic uncertainties in this experiment were in the simulation’s model registration, pulse shape discrimination, and photon detector energy response. As shown in Fig. 2, the BGO and APD spectra agreed well with the scaled spectra predicted by simulation. The branching ratio for the BGO range of 14.1 keV to 782 keV was measured to be 0.00335 ± 0.00005 [statistical] ± 0.00015 [systematic], which agreed with the theoretical value of 0.00308 within 1.7 times the combined standard uncertainty. The branching ratio for the APD range of 0.4 keV to 14 keV was measured to be 0.00582 ± 0.00023 [statistical] ± 0.00062 [systematic], which agreed with the theoretical value of 0.00515 within 1.0 times the combined standard uncertainty.

In summary, we have reported the first precise measurement of the radiative decay of the free neutron spanning three orders of magnitude in photon energy using two different detectors. As the precision is limited by systematic effects, the significantly better understanding of these effects obtained in this experiment provides a path towards an improved experiment with an uncertainty below 1 %. A future experiment could be considered that eliminates the magnetic field, which would allow for particle tracking and improved detection-volume definition. In addition, photon detectors with better proportionality could be implemented, and improvements in low-energy proton detection would allow better identification of proton and electron events. Utilizing a higher intensity cold neutron source should significantly improve the ability to study systematics while maintaining high statistical precision.

References

Ternary systems composed of two immiscible A and B homopolymers and a corresponding AB diblock copolymer are characterized by rich phase diagrams containing numerous morphologies and exhibiting an extraordinary range of structural dynamics. Under appropriate conditions such A/B/AB three-component mixtures will self-assemble into a thermodynamically stable polymeric bicontinuous microemulsion (BuE) with structural dimensions ranging from 10 nm to 500 nm. The polymeric BuE is globally isotropic, but contains locally correlated domains of A/B homopolymers mediated by AB diblock copolymers at the interface [1]. This fascinating state of molecular organization forms through a complex combination of interactions, and a comprehensive understanding of the BuE formation has yet to be realized.

Polymeric systems are very well suited for studying the fundamental nature of the BuE state. Judicious choice of the A and B polymers provides the advantage of small-angle neutron scattering (SANS). We utilized a saturated hydrocarbon system comprised of poly(cyclohexylethylene) (C) and poly(ethylene) (E) homopolymers, and the corresponding CE diblock copolymer, in order to capitalize on this advantage [2].

We have used a combination of SANS and dynamic mechanical spectroscopy to reveal the structural and dynamical features that govern the BuE over a large (80 °C) temperature range [2]. Figure 1 summarizes schematically what we have deduced regarding the equilibrium structure that emerges as the C/E/CE mixture is cooled from a mean-field homogeneous state at high temperatures, to a fluctuating, highly structured, bicontinuous morphology at temperatures below approximately 150 °C (Tc).

As the temperature is reduced, the interfacial area per diblock copolymer chain of the BuE approaches that of the neat lamellar (LAM) diblock copolymer. With increasing temperature, the diblock-rich interface swells through homopolymer infiltration [2].

The structure of the BuE was evaluated over the temperature range 125 °C to 200 °C using SANS. As seen in Figure 2, the mixture produces a single prominent peak at all temperatures, which changes in intensity by two orders of magnitude and broadens between the highest and lowest temperatures. A nearly flat incoherent background intensity, estimated based on the weighted average of the scattering obtained from the pure homopolymers, was subtracted from the acquired data, resulting in Figure 2. The background corrected scattering patterns were fit with the Teubner-Strey (T-S) model [3],

\[ I(q) = \frac{1}{a_2 + c_1 q^2 + c_2 q^4} \]

where \( q = 4\pi \lambda^{-1} \sin(\theta/2) \) (\( \lambda \) is the wavelength, and \( \theta \) is the scattering angle), and \( a_2, c_1, c_2 \) are fitting coefficients. We obtained good agreement between the SANS results and the T-S model over a large q-range, as seen in Figure 2. The model fails to quantitatively reproduce the coherent scattering intensity for \( q > 0.04 \) Å\(^{-1} \), which is attributed to Gaussian coil scattering (\( I(q) \sim q^{-2} \)) due to the hydrogen labeled C (h-C) blocks of the CE diblock copolymer, a consequence of the imperfect contrast matching with the deuterated C (d-C) homopolymer.

From the SANS data in Figure 2, we were able to quantitatively determine the temperature-dependent density of the CE diblock copolymer at the C/E homopolymer interface. To do this, we first estimated the interfacial area per diblock copolymer chain (A_\text{i}) from estimates of the interfacial area per unit volume (S) of the BuE. A_\text{i} is related to S for the BuE, and to the LAM and disordered (DIS) states in the CE diblock copolymer. S can be extracted from any 2-phase system using Porod’s law and the scattering invariant [4]. However, the experimental SANS

\[ A_\text{i} = \frac{1}{\rho_s} \int_0^\infty I(q) \, dq \]

where \( \rho_s \) is the scattering density.

\[ \rho_s = \frac{1}{\rho_g + \rho_q} \]

\[ \rho_q = \frac{1}{\rho_g} \frac{1}{\lambda^2} \int_0^\infty \frac{I(q) \, dq}{q^2} \]

as described in [4].
data at high $q$ (Figure 2) are dominated by scattering from the h-C blocks within the d-C homopolymer domains and by contributions from the incoherent background. This precludes reliable extraction of $S$ using a direct application of Porod’s law. Therefore, we have taken advantage of the excellent quality of the T-S fits to the SANS data and used these fitted functions to estimate the scattering invariant, and to calculate $S$ and $A_c$, assuming these functions apply over all values of $q$.

For comparison, we have estimated $A_c$ for the neat CE diblock copolymer in the LAM and DIS states for comparison with the BµE, using $S_{LAM} = q^*/\pi$ and $S_{DIS} = 0.5q^*$. Values of $q^*$ were determined from SAXS data obtained from previously reported work [5], and the associated $S$ values were converted to $A_c$ and are plotted in Figure 3. Remarkably, the area per block copolymer chain for the BµE asymptotically approaches that of the CE chains in the undiluted LAM morphology in the low temperature limit. Hence, we conclude that cooling the ternary mixture deep into the bicontinuous channel, $T << T_x$, leads to the expulsion of homopolymer from the interfacial region as illustrated in Figure 1a.

These results offer new insights regarding the local properties of the interface and the extent of polymer intermixing in the BµE, as summarized in Figure 1. Although the BµE is globally disordered at all levels of segregation, the molecular environment of the interface resembles that of the neat CE diblock copolymer in the LAM morphology at lower temperatures; the interface becomes saturated with block copolymer, largely excluding the C and E homopolymers from the interfacial region, creating a situation analogous to the dry brush limit. These findings provide fresh insights into the thermodynamic driving forces responsible for the formation of BµEs and highlight opportunities to better understand this fascinating state of self-assembly.

References

Polymer nanocomposites are soft materials composed of a bulk polymer matrix with dispersed nanoscale organic/inorganic particles that are added to modify and improve the mechanical, optical, electrical, and/or thermal properties of the polymer matrix. Driven by the need to develop functionally superior polymer nanocomposites, significant effort has been directed towards linking the molecular-level design of the nanoparticles and polymer to the resulting polymer nanocomposite morphology and understanding the thermodynamics driving the morphology. One way to tailor the composite morphology, specifically dispersion or aggregation of the particles in the polymer matrix, is to densely graft the nanoparticle with polymer chains (graft chains) that are chemically identical to the matrix polymer. Past simulation and experimental studies have shown that the delicate balance of enthalpic and entropic driving forces arising from the interplay of graft and matrix polymer molecular weight ratios, particle size or curvature, grafting density, flexibility of graft and matrix polymers, dispersity in graft and matrix molecular weights dictates the phase transition from dispersed to aggregated states [1-5].

Previous studies have also delineated the connection between the dispersion-aggregation transition to the extent of mixing of the graft and matrix polymer chains [1-5]. When the graft chains are wet (dewet) by the matrix chains, the nanocomposite is driven towards dispersed (aggregated) morphologies. Furthermore, when the graft and matrix polymers are chemically identical, the graft chains are wet by matrix chains and as a result dispersed morphologies are observed only at high graft to matrix polymer molecular weight ratios. Many applications where particle dispersion is desired, however, require matrix chains of fairly large molecular weights which then require long graft chains to achieve a high graft to matrix polymer molecular weight ratios needed for wetting. Grafting large molecular weight polymer chains on nanoparticles is a challenge synthetically, and the large graft chain molecular weights also limit the particle volume fraction in the composite. Thus, there has been a need for new molecular-level design rules that enable wetting of the grafted layer and in turn, particle dispersion even at low graft to matrix polymer molecular weight ratios. One such design rule is to choose graft and matrix chemistries with attractive interactions between the graft and matrix monomers, so as to energetically drive the matrix chains to wet the graft chains even at low graft to matrix molecular weight ratios. In our recent work, using coarse-grained simulations and small angle X-ray and neutron scattering (SAXS and SANS) experiments we studied polymer nanocomposites where the graft-matrix polymer pair exhibit lower critical solution temperature (LCST) behavior, driving the composite to exhibit dispersed morphologies even when the graft molecular weight was smaller than the matrix molecular weight [6]. Interestingly, this process revealed an unexpected result about the coupling between the wetting-dewetting and dispersion-aggregation transitions. We found that in chemically dissimilar graft-matrix polymer nanocomposites, the wetting-dewetting transition occurs gradually with increasing temperature and is distinct from the sharp dispersion-aggregation (phase separation) transition, unlike other work with chemically similar graft-matrix nanocomposites where the two transitions are treated analogously.

In this recent work, the coarse-grained molecular dynamics (CGMD) simulations used a generic model that represents chemically dissimilar graft-matrix polymer pairs that exhibit...
a LCST phase behavior. The experiments focused on a specific system of deuterated polystyrene (dPS) grafted silica nanoparticles (diameter = 15 nm) in a poly(vinyl-methyl-ether) (PVME) matrix as dPS-PVME blends have been shown to exhibit miscibility at room temperature, and a LCST phase behavior with increasing temperatures. In the simulations, the dispersion to aggregation transition was characterized both using simulation snapshots rendered with visual molecular dynamics (VMD) [7] as well as partial structure factors which showed an upturn with increasing temperature as $q \rightarrow 0$, indicative of the onset of particle aggregation. Since the simulations were run at discrete temperatures, the dispersion-aggregation phase transition was marked as the temperature where the onset of the low-$q$ upturn in these partial structures was seen. The low-$q$ value of the partial structure factor as a function of temperature exhibited a sharp transition over a small temperature range, indicating a first-order dispersion-aggregation transition (Figure 1a). The extent of matrix chains wetting the graft chains was calculated using two different methods: monomer concentration profiles and wet monomer fraction. Both methods concurred that with increasing temperature the wetting to dewetting was gradual and onset of dewetting occurred at temperatures below the dispersion to aggregation transition (Figure 1b).

To complement the simulations, SAXS and SANS studies were conducted as a function of temperature on critical volume fraction blends of 226k PVME (80 % by volume) with 33k dPS-grafted silica particles (grafting density = 0.7 chains/nm$^2$). These scattering techniques provide structural information that covers a broad range of length scales and enabled a direct comparison to the simulation results. Since the X-ray contrast between the polymers and nanoparticles in the scattering volume, the bulk phase behavior (and aggregation) of the dPS-grafted silica in PVME was monitored using the low-$q$ behavior in SANS. Figure 2 shows the results from both SAXS and SANS experiment and confirm the conclusions from simulations regarding a sharp first-order dispersion-aggregation transition (blue circles in Figure 2) and gradual wetting to dewetting transition (black triangles in Figure 2).

Simulations showed further that there is a critical extent of wetting which marks the onset of dispersion-aggregation transition; this critical extent of wetting is equal to the extent of wetting of an equivalent chemically identical or athermal nanocomposite (shown in Figure 1b with horizontal dashed lines). Since the wetting-dewetting transition for chemically different graft-matrix composites occurs over a range of temperatures rather than a distinct temperature, there are many “partially wet” and “partially dewet” states that occur between the “fully wet” and “fully dewet” states. This means that one could tune the extent of wetting, i.e., the extent of mixing between the graft and matrix chains, within the aggregated and dispersed morphologies by varying the chemical properties of the system, such as graft-matrix interactions or graft/matrix composition, at specific graft and matrix chain lengths. Fine control over the extent of wetting-dewetting in polymer nanocomposites presents useful control knob for tuning rheological properties that are strongly dependent on the mixing/entanglement of the graft and matrix chains [8-11]. Aside from these exciting new results in the field of polymer nanocomposites, this work also demonstrates the power of simulations and scattering methods to unravel the structure and thermodynamics of complex soft matter that enable engineering and production of new and unique materials with enhanced properties.

### References

Gelation transitions of colloidal systems with bridging attractions

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Structural arrested transitions, such as the glass/gelation transition, describe the change of material from a liquid to a disordered solid state that is associated with a dramatic change of dynamic properties. Yet, despite its importance for a wide range of applications, the physical mechanisms of these transitions remain elusive. Spherical colloidal systems with a short-ranged attraction have long been used as ideal model systems to investigate glass/gelation transitions. While colloidal glass transitions typically take place at very large volume fraction, gelation transitions of spherical colloidal systems usually happen at relatively low concentrations.

A widely studied model colloidal system is the depletion-attraction system, where a short-ranged attraction between large colloidal particles is introduced by adding small polymer/colloidal particles. In general, a depletion attraction system can be considered a binary colloidal system with small solvent particles and large solute particles. There are no attractions between small and large particles in these systems. The added small particles can then introduce an effective attraction between large colloidal particles by an osmotic pressure effect.

Experiments using poly(methyl methacrylate) (PMMA) and polystyrene particles with a depletion-attraction have demonstrated that the gelation transition at a volume fraction of \( \Phi_L = 0.16 \) coincides with the gas-liquid phase transition boundary [1]. It was proposed that the gelation transition of spherical colloidal systems with short-range attraction is due to the frustrated spinodal phase transition and not linked to the percolation transition. Because the equilibrium phase diagram of short-ranged attraction systems does not depend on the microscopic details of a system, the frustrated phase transition has now been widely considered a general theory for the gelation transition of spherical colloidal systems with a short-ranged attraction.

However, there are many experimental systems that can also be considered as binary colloidal systems, where the attraction between small and large particles is not negligible, and in some cases, very strong. The generalization of the physical mechanisms of gelation in a depletion-attraction system to other types of binary colloidal systems has not been carefully examined. Here, we studied the gelation transitions in a binary colloidal system where there is a strong attraction between small solvent and large colloidal particles [2]. The small particles can serve as a bridge to link neighboring particles. By varying the attraction strength between small and large particles, a binary colloidal system can gradually transition from a depletion-attraction system to a bridging attraction system.

The system investigated is composed of large hard polystyrene (PS) spheres \( (R_g = 960 \text{ nm}) \) and small soft poly(N-isopropylacrylamide) (PNIPAM) microgels \( (R_h = 140 \text{ nm}) \) in solvent. Here, \( R_g \) is the radius of gyration determined by neutron scattering (BT5-USANS, NCNR), and \( R_h \) is the hydrodynamic radius determined by dynamic light scattering. PNIPAM microgels can be reversibly adsorbed to the surface of PS spheres [3, 4]. Adding small particles enhances the effective attraction strength between large particles through the bridging of small particles until the attraction strength reaches a maximum value, after which adding more small particles slowly decreases the effective attraction strength [5-7]. This nontrivial dependence of the attraction strength on the small particle concentration results in a fundamental change of the aggregation and gelation behavior compared with depletion attraction systems.

The aggregation at low volume fraction is examined by microscopy as shown in Figure 1. Before adding small particles, large colloidal particles are uniformly dispersed in the solution (Fig. 1a). Adding small particles increases the effective attraction strength quickly resulting in the formation of large aggregates (Fig. 1b).

**FIGURE 1:** Optical microscopy images of dilute mixed suspensions with \( \phi_L = 2.0 \times 10^{-3} \) at various \( \phi_S \). Under the optical microscope, only the large PS spheres are visible because the microgel size is much smaller than the wavelength of visible light.
Further increasing the volume fraction, $\Phi_S$, of small microgel particles results in the large particles re-dispersing as shown in Fig. 1c.

When the volume fraction of large particles, $\Phi_L$, increases, the aggregate size induced by the bridging attraction can be large enough to form percolated clusters resulting in a gelation transition. At a given $\Phi_L$, the gelation transition is confirmed by measuring $G'$ and $G''$ at $0.1 < \omega (\text{rad/s}) < 100$. When $G'$ is larger than $G''$ within the studied frequency range, a sample is considered in a gel state. With increasing $\Phi_S$ at a given $\Phi_L$, a liquid-to-gel-to-liquid transition is observed for many samples. The gelation transition boundaries are identified for suspensions with $\Phi_L$ ranging from 0.01 to 0.35.

In order to locate the experimental gelation boundary in the theoretical phase diagram, the effective interaction between large particles needs to be determined. As the size of the large PS sphere is on the micrometer scale, USANS is ideally suited to probe the inter-particle structure factor, $S(q)$. Fig. 2a shows USANS patterns obtained from mixed suspensions near the gelation boundaries. The USANS data are analyzed based on Baxter’s one component sticky hard-sphere model after taking into account the instrument resolution. The analyzed Baxter’s stickiness parameters, $\tau$, are represented by the reduced second virial coefficient $B_2^*$ with $B_2^* = 1-1/4\tau$. In Fig. 2b, we show the gelation transition boundary (symbols) in the general theoretical phase diagram of a hard sphere system with a short-ranged attraction. These results indicate that the formation of physical gel at intermediate volume fractions follows more closely to the percolation line and deviates from the gas-liquid transition line.

We have demonstrated that in bridging attraction systems, the physical mechanisms of gelation transitions at intermediate volume fractions are clearly different from depletion-attraction systems. Even though at small volume fraction (less than 10 %), the gelation from both systems seems to follow the gas-liquid transition line [6], the gelation transition at intermediate volume fraction is a kinetic driven effect for bridging attraction systems, not directly related to the gas-liquid separation. Our results imply that for many binary colloidal systems, the physical mechanisms of the gelation transition may depend on the nature of the attraction force between the solvent and solute particles. Furthermore, we demonstrate here that tuning the interaction strength between small solvent and large solute particles provides a new way to control the gelation boundary of a system relative to its gas-liquid transition line.

References

Connecting polymer-solvent interactions to structural transformations during solvent vapor annealing of block polymer thin films

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Solvent vapor annealing (SVA) is a powerful technique for directing nanostructure ordering, orientation, and morphology in block polymer (BP) thin films for applications in emerging nanotechnologies such as nanolithographic masks, nanoporous membranes, nanotemplating, and organic optoelectronics. Swelling BP thin films with solvent vapor plasticizes polymer chains and reduces polymer glass transition temperatures ($T_g$), thereby increasing chain mobility and allowing nanostructures to reorganize into well-ordered morphologies. With judicious control over factors including the solvent vapor composition, solvent vapor partial pressure, and swelling/deswelling pathways to influence the thermodynamics and kinetics of the polymer-solvent interactions, one can access a myriad of potential nanostructure conformations not obtainable by traditional thermal annealing alone. Additionally, SVA is ideal for BP systems that are susceptible to thermal transitions and degradation or require infeasible thermal annealing time scales. Therefore, we recently employed a combination of in situ small-angle neutron scattering (SANS) and neutron reflectivity (NR) to elucidate the importance of polymer-solvent interactions on morphology development during SVA of BP thin films [1]. Our results allowed us to glean key insights into the mechanisms of SVA and develop a more predictive approach to target desired nanostructure self-assembly.

Although the effects of SVA on BP self-assembly have been well researched, studies probing how solvent segregation into individual domains governs reorganization kinetics and thermodynamics have not been prevalent. Therefore, we used in situ neutron scattering to quantify the segregation of deuterated benzene ($d$-benzene) into the polystyrene (PS) and polyisoprene (PI) domains of PS-cylinder-forming polystyrene-b-isoprene-b-styrene) (SIS) BP thin films as a function of atmospheric solvent concentration (solvent partial pressure divided by solvent vapor pressure [$p/p_{sat}$]) [1]. Neutron scattering with solvent deuteration provided enhanced polymer-solvent contrast, in comparison to traditional X-ray experiments. From our neutron scattering analysis, we elucidated the full mechanism that describes how the number of stacked domains ($n$) and the out-of-plane domain spacing ($L_z$) changed as a function of film thickness and $p/p_{sat}$ (Figure 1). The key factor in this mechanism was the amount of solvent in the PS block, a commonly ignored parameter that caused a transition between a glassy PS state (kinetically trapped layers) and a non-glassy PS state (mobile layers); the PI domain is always non-glassy at room temperature. Primarily, we found that higher solvent concentrations in the PS domain lowered the $T_g$ below room temperature, which increased the chain mobility and allowed the domains to rearrange and form the low energy domain spacing (modified slightly by commensurability). As the solvent concentration was decreased, $T_g$ increased above room temperature, $n$ was fixed, and $L_z$ decreased as the film de-swelled. Interestingly, although the minority PS domain (cylinders) was the only glassy component at low solvent concentration, the non-glassy PI matrix was kinetically trapped as well and forced to conform to the same compressed $L_z$. This competition between polymer-solvent thermodynamics and kinetics resulted in an unexpected increase in $L_z$ (27 nm to 29 nm) upon deswelling the film from a $p/p_{sat}$ value of 0.93 to a $p/p_{sat}$ value of 0.84, as there was sufficient $d$-benzene in the PS

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domain (51 % by mole and 40 % by mole, respectively) to lower the \( T_g \) of PS below 25 °C and impart chain mobility [2]. Therefore, the polymer chains were able to decrease \( n \) and subsequent incommensurability promoting slightly thicker layers. The inset plot shows how the film thickness and \( L_z \) change as a function of \( p/p_{sat} \). The NR profiles have been vertically offset for clarity.

To understand the cause of the structural transition, azimuthally averaged 1-D intensity profiles from in situ SANS, taken at the NGB 10 m SANS, (Figure 3a) were analyzed to quantify the solvent uptake in each domain as a function of \( p/p_{sat} \) (Figure 3b). Figure 3b revealed that at a \( p/p_{sat} \) value of 0.59, there was not a sufficient concentration of solvent to reduce the PS \( T_g \) below 25 °C (25-30) % by mole [2], and the PS domain transitioned to a glassy state. The \( p/p_{sat} \) value at which the glassy/non-glassy transition occurred matched with the \( p/p_{sat} \) value at which the restructuring mechanism, (measured with NR) changed, providing the final piece to the SVA mechanism.

In summary, we related measurable differences in \( L_z \), \( n \), and film thickness to in-plane and out-of-plane solvent profiles determined with SANS and NR, respectively. The ability to add polymer-solvent contrast (via \( d \)-benzene) allowed us to relate both polymer-polymer and polymer-solvent interactions to the reorganization of nanostructures during SVA. Thus, we determined how solvent preferentially diffuses into individual domains, tracked solvent diffusion and nanostructure reorganization as a function of \( p/p_{sat} \), and monitored the kinetic trapping of nanostructure reorganization with solvent removal. Finally, we demonstrated that \( L_z \) can be controlled by manipulating the solvent content in the film and the swelling/drying pathway. These outcomes help define several of the underlying mechanisms that govern self-assembly in BP thin films subjected to SVA, such as the mobility required to restructure the domain lattice, the impact of surface and interfacial roughness on commensurability constraints, the trapping of solvent in the film as a function of polymer mobility, and the selectivity of polymer and solvent at the free and substrate surfaces, which can facilitate the prediction of ideal solvent annealing conditions depending on the objectives.

### References


Nano-deformation of sphere-forming thermoplastic elastomers during uniaxial extension

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Elastomers’ mechanical properties are greatly influenced by their microstructural features, e.g., cross-link density, type of crosslinking (physical or chemical), concentration and morphology of hard domains and/or nanofillers, etc. Therefore, engineering new elastomers with improved properties require deep understanding of the interrelations between mechanical response and microstructure evolution during deformation. To achieve this, in-situ nanostructure probes integrated with mechanical probes are needed. We present a method that combines small-angle neutron scattering (SANS), as the microstructure probe, with a commercial Sentmanat extensional rheometer (SER) that provides uniaxial deformation and measures the stress response from the sample (see Fig. 1) [1].

Due to their commercial applicability, thermoplastic elastomers (TPEs) consisting of ABA-type triblock copolymers with styrenic end blocks and a rubbery middle block have been extensively studied. Most deformation studies of these TPEs are focused on systems with cylindrical and lamellar morphology [2], and very few on sphere-forming systems [3-5]. Among those studies, there is no consensus on whether the micro-deformation is affine or non-affine and whether the glassy domains deform or not. To elucidate such questions, we performed in-situ tensile-SANS measurements of sphere-forming blends of a SIS block copolymer with a low molecular weight deuterated polystyrene (dPS) during uniaxial deformation.

Figure 2 shows the stress-strain curve of the SIS/dPS blend measured in the rheometer, along with the 2D SANS profiles measured during the deformation. The initially isotropic circular profile (corresponding to a body-centered cubic lattice) becomes elliptical in the elastic and yield regimes, which indicates that the lattice is extended in the stretching direction (SD) and compressed in the transverse direction (TD). A new microstructural feature was observed at high elongations, namely the formation of quadrulobe patterns. These were previously observed in cylinder forming block copolymers [2, 6], in which their formation are associated to chevron-type arrangements of the cylinders. In our system the quadrulobes originate from the rearrangement of the glassy spheres into strings that orient into preferential angles inclined towards the stretching direction, as shown in the micrograph in Fig. 2.

Stress unloading is accompanied by the disappearance of the quadrulobe pattern and by the reduction of the anisotropy of the ellipsoidal scattering shapes. This indicates that the “oriented stings” configuration is not stable and the structure reverts to

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the equilibrium BCC lattice structure once the stress is removed. This occurs due to the interconnectivity of the glassy domains via the rubbery middle block, which in turn is responsible for the elastic response of these materials. After unloading and complete removal of stress, a remnant deformation (evidenced by permanent anisotropy in the scattering peaks) is observed. This permanent deformation contributes to the permanent set measured macroscopically.

In order to determine the transition from affine to non-affine deformation, azimuthally averaged SANS intensities of circular sectors (with arc angle of 20°) along SD and TD are computed for each strain probed during loading and unloading. 2D SANS profiles for the 5% dPS/SIS blend at Hencky strain $\varepsilon_H = 0.5$ is shown in Fig. 3 with the circular sectors in SD (90°) and TD (0°) indicated as shaded areas, along with the azimuthally averaged sector 1D SANS profiles. The $q$-values corresponding to the scattering peaks measured in the sectors parallel to SD and TD are indicated as $q^*_\text{SD}$ and $q^*_\text{TD}$, respectively. For $\varepsilon_H = 0$, $q^*_\text{SD} = q^*_\text{TD} = q^*_0$, which confirms that the initial structure is fully isotropic. Also expected is that $q^*_\text{SD} < q^*_\text{TD}$ at $\varepsilon_H = 0$, indicating an increase in inter-sphere spacing along SD and a contraction of the spacing along TD, as illustrated in the schematic drawing in Fig. 3. The changes in magnitude of the two vector components, with respect to the un-stretched state, are given by $q^*_0 / q^*_\text{SD}$ and $q^*_0 / q^*_\text{TD}$, respectively. If the rearrangement of the polystyrene spheres is affine, then the ratio between the changes in length ($L$) and width ($W$) of the film must be the same as that between the vector component in SD and TD. To verify this, plots of $\ln(W/W_0)$ versus $\varepsilon_H = \ln(\lambda) = \ln(L/L_0)$ (lines) along with plots of $q^*_0 / q^*_\text{SD}$ versus $q^*_0 / q^*_\text{TD}$ (symbols) are given in Figure 3 (lower panel). The deviation from the theoretical slope of $-1/2$ indicates that the deformation is non affine above $\varepsilon_H > 0.3$. Hence, the transition between affine and non-affine deformation is determined to be at $\varepsilon_H = 0.35$. This transition preludes the appearance of quadrulobes in the SANS profiles which, as discussed above, is associated to the BCC-to-Chevron transition, and hence, non-affine deformation is not surprising.

Combining mechanical testing with SANS provides a very powerful tool to elucidate the structural origins of elastic response of nanostructured elastomers. We have shown that strain-hardening, hysteresis, permanent set, as well as affine to non-affine deformation transition are the result of rearrangement in the nanostructure of the sphere-forming block copolymer TPE studied [1]. These studies are being extended to other types of polymeric systems, such as polyolefins [7], and polymer melts, which lack contrast for other scattering techniques (e.g., SAXS).

References

Ultralong polymers have remarkable properties that enable drag reduction in pipelines and control of drop breakup. For example, even at low concentrations (= 10 to 100) x 10^{-6} g/g, ultralong polymers (>4x10^{6} g/mol) dissolved in jet fuel reduce the risk of post-crash large, hot fireballs. By inhibiting mist formation, ultralong polymers reduce the droplet surface area through which fuel evaporates and, consequently, reduce the extent and intensity of the resulting fire. The longer the polymers, the more potent they become—and the more vulnerable. Stress accumulates along the chain, particularly in strong flows (e.g., passing through pumps), reaching levels that break the backbone [1]. Using statistical mechanics, we designed end-functional polymers that are individually short enough to survive routine handling and assemble into supramolecules to mimic ultralong polymers. They control mist—but reversibly separate under high stress to avoid degradation. To test the theoretical basis for these effects, small angle neutron scattering (SANS) was uniquely able to provide the necessary information on the supramolecular structure. The results support the theoretical model and open the way to design of further end-to-end associative polymers with unprecedented combinations of properties [2].

Flows through industrial pumps and filters typically break chains to pieces < 0.7x10^{6} g/mol - too short to reduce drag or inhibit misting. We sought to use chains that are near, but shorter than, this limiting length and stick them together into very long, multimillion molecular weight supramolecules—“megasupramolecules” (M_{w} > 4x10^{6} g/mol). There were conflicting demands that might have made it impossible. On one hand, literature shows that increasing backbone lengths beyond 5x10^{6} g/mol disfavors end-association. On the other hand, long chains are needed to disfavor formation of rings, which are ineffective, when used at the low concentrations relevant to fuel additives. To check the feasibility of building ultralong supramolecules at low concentration, we used a statistical mechanical lattice model to calculate the populations of linear and cyclic aggregates of end-associative polymers as a function of the association strength, backbone length, and concentration. The model predicted that using end-association of long chains is feasible—providing the required 50 ppm of megasupramolecules (Figure 1, A)—but only in a small window of parameter space. The backbone length must be long enough that a string of 8-10 reaches the length of ultralong polymers and short enough to not suffer from shear degradation. The association strength must be very strong to drive formation of megasupramolecules—but not too strong, or ineffective circular supramolecules will dominate over linear ones.

We set out to make the predicted molecules with structures suitable for use in fuel. We excluded salt- or metal-mediated associations; however, the required strength of end association (16 kT to 18 kT) was comparable to the strongest previously reported hydrogen-bond “stickers.” We turned to charge-assisted hydrogen bonds, each providing 8 kT to 9 kT. These tertiary amines on each end of the “diacid” (DB) chains and two carboxylic acids on each end of the “dibase” (DA) chains can deliver the needed 16 kT to 18 kT. The model requires individual end-associative chains, approximately ten-times longer than previously examined end-functional “telehelic” chains. Although there was no precedent for making such long telechelics, we were able expand the envelope of accessible chains lengths via two-step ring-opening metathesis polymerization (ROMP), using a chain transfer agent (CTA) to start and end each chain with a functional group. In some cases, the initial end groups (R_1) are subsequently converted to associative groups (R_2) acid- and base-ended chains (Figure 1, B).

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Assembly of DA/DB into large supramolecules is evident in cyclohexane, tetralin, and Jet-A, manifested by increased specific viscosity compared to the nonassociative controls at the same backbone length (Figure 2, A). Static light scattering at a weight fraction of 0.028 % (35 °C) shows supramolecules of $M_w$ 2200 kg/mol (2.2 M, solid circles), which separate into individual units (x) when a small-molecule tertiary amine, TEA, is added (open circles). Curves show predictions from theory for 1000 kg/mol polymers at 1400 x 10^{-6} g/g (solid, associative; dashed, NA). C and D). Impact test in presence of ignition sources (60 ms after impact, maximal flame propagation). Jet-A treated with conventional ultralong polymer 4.2M PIB (mass fraction of 0.35 %) or with end-associative 430k TA PCOD (mass fraction of 0.3 %). “Unsheared” is as-prepared, “sheared” is after ≈ 60 passes through fuel pump.

By using a theoretical model for end-associative polymers, we were able to propose and synthesize polymers capable of self-assembling into long chains in solution and surviving high shear conditions, like repeated pumping. Neutron scattering, light scattering, and specific viscosity all confirm association of these polymers in solution. In practice, these carefully selected associative polymers do provide effective mist control. We verified that these mist control properties are due to the reversible separation of the chains through contrasting associative and nonassociative versions of these polymers, and by comparing the associative polymer’s mist control ability and a commercial long-chain polymer before and after shearing. These associative polymers are able to imitate the behavior of long-chain polymers, yet retain their efficacy despite high stress conditions, making them attractive additives for mist control.

**References**


Dielectric RheoSANS for the simultaneous interrogation of rheology, microstructure, and electronic properties of complex fluids

J. J. Richards, C. V. L. Gagnon, J. R. Krzywon, N. J. Wagner, and P. D. Butler

Introduction

In situ measurements are an increasingly important tool to elucidate the complex relationship between nanoscale properties and macroscopic measurements. One important example is the electrical and mechanical properties of carbon black slurries. While carbon based nanocomposites have been studied for decades, an emerging application is their use as an electrically percolating network in semi-solid flow battery electrodes [1]. In this application, electrical conductivity must be maintained while the electrode is continuously pumped through an electrochemical flow cell. Under these conditions, it is highly desirable to maximize the conductivity of these suspensions while reducing their viscosity in order to minimize pumping losses. Our hypothesis is that the relationship between viscosity and conductivity is a direct product of material microstructure and colloidal interactions. To test this hypothesis, we seek a way to measure the electrical, mechanical, and microstructural response of carbon particles under arbitrarily complex deformations. To accomplish this, we have developed a new Dielectric RheoSANS environment.

The instrument consists of a Couette geometry mounted on an ARES G2 strain controlled rheometer enclosed in a modified Forced Convection Oven (FCO) shown Figure 1a. The carbon black slurry is confined between concentric titanium cylinders that are nearly transparent to neutrons. Both cylinders are electrically isolated from the rheometer. In a Dielectric RheoSANS experiment, the impedance response is measured by an impedance-capacitance (LCR) meter and stress response is measured by the rheometer. The control scheme for this procedure is shown in Figure 1b and is made possible through a programmable Labview interface that measures signals from the LCR meter and the rheometer. An analog triggering protocol synchronizes those measurements to the SANS event mode acquisition. At the end of a preprogrammed set of shear conditions, the entire rheological, electrical and microstructural characteristics of the sample can be reconstructed and time binned in order to quantify changes in microstructure as a function of both the shear conditions and time.

An example raw data output from Dielectric RheoSANS experiment from a 3 % by mass Vulcan XC72 sample dispersed in hydrogenated propylene carbonate is shown in Figure 1c. From top to bottom Fig. 1c shows the rheological, electrical, and microstructural response of a single sample throughout the course of an acquisition. Using this approach, we are able to capture the liquid to gel transition that takes place as shear stress imposed on the carbon black suspension drops below the yield stress of the bulk gel. The instrument design and findings resulting from initial testing will appear in forthcoming publications [2, 3]. While the Dielectric RheoSANS instrument was developed to answer important questions related to flowability of carbon black suspensions, it has the potential to expand the study of other complex suspension behavior, and will soon be available for use within the user program.

References

The scattering vector range of small-angle neutron scattering using pinhole geometry may be extended to $10^{-3}$ Å⁻¹ using a double perfect crystal instrument [1]. The poor resolution in the direction normal to the scan direction enables increased intensity, but the slit-smeared data requires a correction before concatenation with the SANS data. The desmearing algorithm is valid only for azimuthally symmetric scattering, such that the scattering in the scan direction and the slit direction are the same. This presents a problem for the analysis of USANS data of asymmetric scattering systems. We offer a method [2] to modify asymmetric data that follow a power law such that the USANS data concatenate well with that obtained using pinhole SANS.

SANS measurements on thin shale sections cut both along the bedding plane and normal to bedding show power law scattering with an exponent $n$. The scattering from shale cut parallel to the bedding plane has azimuthal symmetry with circular contours on the two-dimensional detector that are averaged to obtain intensity $I(Q)$ shown by the brown curve labeled X in Figure 1a. The perpendicular-cuts scattering has elliptical contours. Sector averages are taken in directions parallel (Y curve in blue) and normal (Z curve in red) to bedding for the perpendicular-cut sample. Note that curves X and Y are coincident. The R curve in green is for the perpendicular-cut sample rotated continuously in the incident beam.

We assume that the $Q$ dependence of the scattering is separable from the azimuthal dependence and the intensity may be written

$$I(Q, \phi) = A \phi Q^{-n} \cdot \left[ a^2 \cos^2 \phi + b^2 \sin^2 \phi \right]^{-n},$$

where $\phi$ is the azimuthal angle relative to the normal to bedding. In the $\phi = 0$ (or Z) direction, $I_z(Q) = A \phi Q^{-n} \cdot a^2 Q^{-n}$, and the $\phi = \pi/2$ (or Y) direction, $I_y(Q) = A \phi Q^{-n} \cdot b^2 Q^{-n}$. The factor $a/b$ corresponds to the ratio of the long and short semi-axes of the elliptical isointensity contours. The Z plot may be made coincident with the Y plot by multiplying the intensity values by $(b/a)^n$.

The slit-smeared USANS data also have power law scattering with an exponent $m$, such that $m = n-1$. Figure 1a also shows the slit-corrected USANS results indicating that the desmearing of the X and R data results in a smooth transition when concatenated with the SANS data. On the other hand, the Y curve is no longer coincident with the X curve. When the two datasets are joined, the desmeared Y data have a positive shift in intensity, while the Z data have a negative shift.

An elliptical contour has a corresponding circular contour of radius $r = (ab)^{1/2}$, the geometric average of the two semi-axes of the contours obtained from the SANS measurement. We multiply the Y intensity data by a factor $(b/r)^m = (b/a)^{m/2}$ and then perform the desmearing. Figure 1b shows that the modified USANS Y intensity concatenates well with the SANS Y data and is consistent with the USANS X data. Similarly, multiplying the USANS Z intensity data by a factor $(a/r)^m = (a/b)^{m/2}$ before desmearing results in the modified data having good concatenation with the SANS data. This procedure results in an intensity for asymmetric scattering that is consistent over the wide $Q$ range offered by the combined measurement.

**References**

Application of small-angle scattering data to improve biomolecular docking success rate using Rosetta

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Biological macromolecules often associate to form complexes in solution. Obtaining information on the orientation of each protein partner within a complex can help determine functionality in applications such as actin filaments, bacterial flagellar filaments, design of antibody complementarity determining regions (CDR) for targeted antigen epitope binding, and protein oligomerization. Most algorithms used to model small-angle scattering (SAS) data of protein complexes rely on the use of dummy-spheres and do not account for the physics of the system. One method that is widely used to predict protein complex formation is the Rosetta suite of “docking” computational physics programs. Prediction of protein-protein docking can be particularly challenging when no experimental data on the system is known. Hence it is necessary to do an initial global search of relative protein configurations, where many thousands of docking decoy structures are required. Typically, either shape complementarity or an interaction energy for the two partners is used to calculate a docking score for each relative configuration. We have developed a protocol [1], to be implemented as part of the SASSIE program [2], which combines predictive capabilities from molecular docking simulations combined with an analysis of experimental SAS data. This method will benefit both the Rosetta docking and SAS communities.

Most protein-protein docking strategies employ an initial low-resolution stage (LR), where the proteins are treated as rigid bodies where the amino acid side chains are not permitted to move with respect to each other. This is then followed by a high-resolution stage (HR) within the local configuration space of each decoy from the LR search, which is then treated at a level of higher accuracy. Side chain atoms are allowed to move in this stage. For HR docking, a near-native structure is defined by decoys having an interfacial root mean-squared deviation (RMSD), relative to the native structure, of less than 4.0. Docking success is then defined by the occurrence of least three near-native decoys within the top five (interfacial) scored HR decoys.

Our protocol involves first performing a LR scan to generate tens of thousands of decoy structures. Four protein structures were selected for initial benchmark study. For one of these protein-protein complexes, the neuroligin-1/β-neurexin protein complex, experimental SAS data was available [3]. Theoretical SAS profiles are then calculated [2] for each structure and the resulting I(q)-plots are compared to experimental SAS data using reduced χ2. The χ2 values are used along with the set of docking scores to divide the initial set of LR docking decoy structures into four sets.

It is found that the set representing (both) high docking score and small χ2 generate the largest number of docking successes when those decoys are used as input structures for the subsequent HR docking. This is illustrated in Fig. 1A. For the case of the neuroligin-1/β-neurexin protein complex, Fig. 1B shows the shape model obtained from a standard analysis of SAS data, superposed on the native structure, which has subsequently been solved [4]. Fig. 1C shows a model of one docking success, again superposed on the native structure. Comparing Fig. 1B to 1C represents the extent to which the shape model misplaces the orientation and relative position of the neurexin ligand by comparison to the structure representing a docking success that shows much better alignment relative to the known native structure.

These results show that SAS data may be used to assist the docking user in protein-protein docking with additional means of selectively filtering false positives among a set of decoy structures generated by a global docking search and provides the SAS user with a modeling strategy that includes an accounting of physical interactions.

References

A second-generation low-background gamma-ray spectrometer

R. M. Lindstrom

Nuclear analytical methods often need to be pushed to maximum sensitivity. Detection limits in gamma-ray spectrometry are improved by increasing the efficiency of the detector and by decreasing its background. A low-background gamma spectrometer system in a dedicated laboratory above ground at NIST has been in use for sensitive radioactivity measurements for more than twenty years [1]. Because the germanium detector, named Ty, is built of selected materials and is housed in an optimized shield of selected lead, its background is dominated by cosmic radiation even though it is located in the Reactor Building. Most of the background rate consists of a broad continuum from high-energy cosmic-ray muons. These muons also generate fast neutrons in the detector shield, which undergo inelastic scattering in the materials of the instrument, giving characteristic gamma peaks from isotopes of Fe, Cu, Pb, and the Ge detector itself.

One of the most useful criteria for selecting and using a Ge gamma-ray detector, in that it incorporates all the specifications of a spectrometer, was proposed by Cooper [2]. It may be rewritten [3] for the case of very low activity as

\[
D(E) = \frac{A}{t \varepsilon(E) \Gamma(E)} \left[ \left( 2t B(E) b R(E) + \frac{A^2}{4} \right) + \frac{A}{2} \right]
\]

where

- \(D(E)\) = minimum detectable disintegration rate, Bq
- \(A\) = reciprocal of the desired fractional precision (= 10 for 10 %)
- \(t\) = counting time, s
- \(\varepsilon(E)\) = detector efficiency, counts/photon
- \(\Gamma(E)\) = gamma-ray yield, photons/decay
- \(R(E)\) = detector resolution (fwhm), keV
- \(b\) = peak integration width, in multiples of the resolution \(R\)
- \(B(E)\) = background rate, counts s^{-1}keV^{-1}

Another established low-background detector in this laboratory is operated in anticoincidence with a surrounding NaI scintillator. This procedure reduces the muon continuum by an average factor >15 between 500 keV and 2000 keV. Although the detection limit for single-photon nuclides is indeed improved by about the expected factor of four, this scheme is unsuitable for measuring nuclides with cascade decays: the detection limit for ^{60}\text{Co} is in fact worse by a factor of two when anticoincidence is applied. In addition, with massive NaI closely surrounding the detector, this system is usable only for small-sized sources.

FIGURE 1: The second-generation detection system installed in the dedicated low-background counting room. The new Ge detector “Glen” is seen in the center of the shielding.

A new second-generation detector system is being constructed, with four improvements over the 1990 Ty detector.

1) The relative efficiency of the new Ge detector, named Glen, is 110 %, nearly three times that of the Ty system, at once improving the detection limit by more than 50 %.

2) The detector is shielded by 15 cm of pre-1945 iron rather than lead. Because the production rate of (μ, n) neutrons per kilogram of shielding is proportional to the atomic mass \(A\), the fast-neutron flux is \(6 \times 10^{-3}\) cm^{-2}s^{-1}, a factor 5 lower than in the lead shield of the Ty detector. There is ample room inside the 160L shield for bulky samples.

3) An umbrella of plastic scintillators covers three adjoining exterior faces of the shield, and is operated in anticoincidence with the central Ge to cancel the muon continuum by a factor of eight. Most of the remaining peaks in the background spectrum are due to radon, which is reduced by displacing the air inside the shield, either with nitrogen-filled pillows or by venting the detector Dewar into the shield.

4) The all-digital data acquisition system is capable of time-stamped list mode recording, enabling the signal shaping and logic timing to be optimally tuned.

As a result of these updates, the detection limit (or alternatively the required counting time for a given statistical uncertainty) has been improved by a factor of five over the old low-background spectrometer, the sample shape and size requirements are relaxed, and the background spectrum contains fewer interfering peaks.

References

μRheoSANS for measurement of complex fluids structure at high shear rates

J. Weston, 1 D. Seeman, 2 S. D. Hudson, 2 and K. M. Weigandt 2

Small angle neutron scattering measurements of complex fluids undergoing shear deformation have significantly enhanced our understanding of the structure-rheology relationships in materials [1]. Most rheoSANS measurements are made using Couette geometries due to the relatively simple flow field and the constraints of scattering geometry. However, Couette shear cells are typically limited to maximum shear rates on the order of $10^4 \text{s}^{-1}$. This is well below some commonly encountered industrial applications such as spraying, injection, extrusion or lubrication processes, with shear rates approaching or above $10^6 \text{s}^{-1}$. We have begun to develop thin slit rheometers for simultaneous SANS and rheology measurements in order to characterize structural changes at these much higher shear rates.

A prototype thin slit flow cell that is 100 µm deep, 8 mm wide, and 35 mm long has been adapted for use in a neutron beam (Figure 1). Flow is driven by external rate controlled pumps (typically syringe pumps). Pressure sensors are installed inline before and after the flow cell to measure the pressure drop. The pressure drop is used to calculate the viscosity as a function of shear rate during the SANS experiment. The current device is suitable for measurements with pressure drop less than 700 kPa, but ongoing development is aimed at reaching pressures as high as 70 MPa [2]. Preliminary experiments used a 33 mmol/L cetylpyridinium chloride and 20 mmol/L sodium salicylate wormlike micelle solution in D$_2$O. A gear pump was used to recirculate the solution through the µRheoSANS apparatus and a thermal jacketed reservoir was used to extract excess heat generated from the pump motor and viscous heating. Example reduced 2D scattering patterns are plotted in Figure 2, left and center.

However, Poiseuille flow is more complicated than Couette flow and the shear rate is not constant through the sample. In fact, it varies from 0 s$^{-1}$ in the center to a maximum at the wall (which increases with flow rate). Thus, the scattering represents an average structure over all of the shear rates in the flow cell. Knowing that, for continuous fluids, the shear stress ($\tau$) decays linearly from a maximum at the wall to zero in the center of the channel we can deconvolute and isolate the scattering from the near wall sample (as shown in the equation) so long as there is scattering data from two different flow rates ($Q$). Examples of the deconvoluted high shear scattering data is shown in Figure 2 (right).

$$I_{q_x,q_y}(\text{wall}) = \frac{1}{1 - \frac{\tau_{\text{wall},n}}{\tau_{\text{wall},n-1}}} \left[ I_{q_x,q_y}(Q_n) - \frac{\tau_{\text{wall},n}}{\tau_{\text{wall},n-1}} I_{q_x,q_y}(Q_{n-1}) \right]$$

As expected, at low flow rates when the scattering is isotropic applying the deconvolution does not have any effect on the data. Similarly, at very high flow rates where the data is highly aligned in all but smallest region near the center of the channel, the deconvolution yields 2D data very similar to the original data set. However, at intermediate flow rates when the sample is transitioning from an unaligned to a maximally aligned state, there is significant variation in the micelle structure throughout the channel. Upon applying the deconvolution, it is qualitatively very clear that the near wall structure (high shear rate) is much more aligned relative to the bulk average structure at these flow rates.

References


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**Reliability and Availability of the Reactor**

The reactor operated 265 days during FY 2016, achieving a reliability of 96.5%. The 4.4 days that were lost were due to three separate events: 1) a dropped fuel element, 2) the failure of an instrumentation power supply due to lightning and 3) a failure of a PLC in the cold source. Some of that lost time was made up by extending the reactor cycles.

**Liquid Deuterium Cold Source Status**

The NBSR neutron source provides beams of thermal and cold neutrons for research in materials science, fundamental physics and nuclear chemistry. From its initial design, a large, 55 cm diameter beam port was included for the installation of a cold neutron source, and the NCNR has been steadily improving its cold neutron facilities for more than 25 years. Monte Carlo simulations have shown that upgrading to a liquid deuterium (LD$_2$) source will provide an average gain of 1.5 between 4 Å and 9 Å with respect to the existing liquid hydrogen cold source, and a gain of 2 at the longest wavelengths. The conceptual design of the proposed source was presented in the 2012 NCNR Annual Report. Funding for the refrigerator and the cold source upgrade has been granted by the National Nuclear Security Administration of the Department of Energy as a mitigation strategy to offset the anticipated 10% loss in neutron flux when the NBSR is converted to low-enriched uranium (LEU) fuel. The NCNR has been actively preparing for this fuel transition.

Many of the components necessary for the LD$_2$ source have been procured. To manage the heat load on the LD$_2$ cold source, a new, 7 kW helium refrigerator is being installed to provide the necessary cooling capacity. It is expected that acceptance testing will be completed later this year. The 16 m$^3$ ballast tank to store the deuterium at ≈ 4 bar when the refrigerator is not operating has been installed outside the guide hall; this provides a passively safe response to a refrigerator failure. A pair of deuterium condensers was obtained (Figure 1) and has since been integrated into two condenser assemblies (one spare) with completion of their vacuum and He containment jackets.

In FY 2017, it is expected that a final subcontract will be awarded for the turbine installation, testing and commissioning of the refrigerator. The new refrigerator will be used to operate the existing cold sources after its cooling capacity has been demonstrated. Also in FY 2017, detailed designs of the cryostat assembly components will be completed and the fabrication of prototype vessels for testing will begin. Upon successful completion of tests on the prototypes, two complete cryostats will be fabricated. Because of contracting issues, it is now expected that installation of the LD$_2$ source will not occur before 2021.

**Feasibility Studies for a Replacement Reactor**

The NBSR, first critical on the 7th of December 1967, is currently licensed to operate until 2029, and then it will likely be re-licensed for 20 more years. The reactor will eventually need to be replaced however, to meet the ever-growing demand of the neutron scattering community. The demand is particularly great for cold neutron beams; more than 70% of the research at the NCNR uses cold neutrons.

A reactor replacement study was initiated, and efforts to design a new research reactor optimized for cold neutron sources are currently underway. The primary purpose of the proposed new reactor is to provide high intensity cold neutron beams for scientific experiments. An innovative horizontally split compact core cooled and moderated by light water while reflected by heavy water is being investigated at this stage to achieve better flux performance [1]. The new reactor was designed for 20 MW thermal power and a 30 day refueling cycle for an equilibrium core condition to provide a cost-effective research facility.

A cut-away view of the reactor design is shown in Figure 2, illustrating the reactor components. An innovative horizontally split core scheme is employed in the design such that a thermal flux...
The core is cooled and moderated by light water and surrounded by the heavy water reflector. The core halves are enclosed in two zirconium core boxes that separate heavy water and light water. Two vertical liquid deuterium cold neutron sources are placed in the flux trap located in the north and south sides of the core. Two CNS beam tubes are connected to the CNSs with guides pointing north and south. Four tangential thermal beam tubes are placed in the east and west sides of the core at different elevations. The split core consists of 18 MTR-type fuel elements in two horizontally split regions. Each region consists of 9 fuel elements and represents one half of the reactor core.

The most important figure of merit to evaluate the performance of a cold neutron source is the “brightness” of the source in the direction of the guides to various instruments. The calculated brightness of the vertical CNS in the split core compared to the actual performance of the existing large liquid hydrogen (\(\text{LH}_2\)) CNS at the NCNR clearly shows that substantial gains can be achieved in brightness for the new design. Since the present NIST liquid hydrogen CNS has comparable performance per MW with most existing cold sources, the preliminary results indicate the performance of the vertical CNS in the split core has significant gains (a factor of \(\approx 3\)) compared to nearly all currently available cold neutron sources. Some preliminary efforts made to optimize the CNS geometry indicate another 20 % to 40 % gain is possible.

The thermal neutron beam tubes are comparable to the existing NBSR beams. Only four are modelled in the present design. It may be possible to add additional thermal beams, or include one or two larger ports for some thermal neutron guides serving many instruments. The design is in a conceptual phase, and will change as engineering constraints continue to be introduced. A more detailed model, including a primary cooling loop is under development.

Reference

Installations and Upgrades

Two major instrument development projects have dominated the efforts of the RFO group. First, work on the 40 m very Small Angle Neutron Scattering (vSANS) has been accelerating with designs, procurements, fabrications, installation, and testing continuing throughout 2016. By the end of 2016, vSANS will have installed, aligned, wired, and tested the pre-sample neutron beam delivery system, including the velocity selector and neutron/ gamma shielding (bunker), cryogenically cooled crystalline Bi-Be filter, attenuator assembly, polarizer guide, and 11 pre-sample flight path boxes (Figures 1 and 2). The boxes contain the neutron guides, circular apertures, slit apertures, and magnetic guide fields, all under computer control. The 64 motors required is the largest motion control installation at the NCNR to date. The tube detectors arrays have been tested and the histogramming and management software has been written. However, contractor delays have pushed the delivery of the detector vessel back to late 2016, delaying the wiring and installation of the detectors on the front and middle carriages. The rear detector carriage will support a 2D detector that has been awarded and will be installed as part of phase II in 2017. We anticipate having the first neutrons on detector in April of 2017, the first SANS experiment June 2017, and full polarized beam SANS experiment by January 2018.

Activity at NG1 to prepare for the CANDOR Reflectometer has been ongoing. Physically, the detector test station has been relocated from NG1 to PHADES at NG7 to make room for CANDOR. Power, plumbing, and real estate have been re-configured or moved so that all beam line components from the beam delivery system to the sample position could be installed and aligned. This includes major components such as the converging guide, monochromator, Be/Bi filter, and apertures. Many more parts have been procured and are assembled and tested as they arrive.

The first full scale test of the chromatically optimized neutron detector for the CANDOR instrument was performed on SPINS this year. In this detector array, (Figures 3 and 4) 54 highly ordered pyrolytic graphite (HOPG) crystals are set at different takeoff angles to diffract neutrons into $^6$LiF:ZnS(Ag) scintillator based proportional counters (described in the 2014 Annual Report). The test involved varying the incident energy of the beam entering the array and monitoring the output of the scintillator detectors. The results are consistent with simulation, but have revealed the need for extraordinary precision in assembly and alignment. With the successful testing, efforts have focused on completing the full 30-array detector package.
We anticipate to have the first neutrons on the CANDOR detector September 2017, first specular reflection experiment January 2018, full polarized beam operation March 2018, and non-specular capability available June 2018.

Several other upgrade and installation projects have also been completed in 2016. A new velocity selector for BT-7 has been received from Airbus and all performance testing has been completed. Design and fabrication of all components needed to install the velocity selector is nearing completion, and installation is scheduled for December 2016. The Neutron Spin Echo instrument at NG-A saw performance gains as the helium cooling system was tested and adjusted so the large 8-inch correction coil amperage could be increased from 50 A to 62.5 A and the current in the small and middle correction coils increased proportionally, giving the same proportional increase in the maximum accessible experiment Fourier time.

Helium Spin Filters

The NCNR supports an active program to develop and provide $^3$He neutron spin filters (NSFs) to support measurement capabilities using polarized neutrons. Polarized beam experiments are routinely carried out on the BT-7 thermal neutron triple-axis spectrometer, the small-angle neutron scattering instruments, and the multi-axis crystal spectrometer (MACS). During the past year, the NCNR’s spin filter program serviced 26 user experiments, for a total of 102 days of beam time, 116 bar-liters of polarized $^3$He gas, and 99 polarized $^3$He cells.

The NCNR and the PML have focused on deploying one of the worlds most powerful wide-angle neutron polarization analysis capabilities on MACS. We have implemented a reliable procedure to demagnetize the instrument after the use of superconducting magnets that permits $^3$He relaxation times on MACS close to the intrinsic values observed off-line. Several important polarized beam MACS experiments performed last year benefitted from these long relaxation times, and are yielding important scientific results. We have redesigned and built two new NMR-based $^3$He polarization flippers to address intermittent unreliable behavior in the first prototype device. They have been tested and are reliable, and are available for routine polarized MACS experiments. Figure 5 shows one of the $^3$He NMR flippers, which is a very compact, integrated neutron polarizer and flipper device.

We have expanded the development of the horseshoe-shaped wide-angle cells, which provide polarization analysis of the entire 220° range of scattering angles on MACS with a single analyzer cell. We have fabricated two such cells, available for routine polarized MACS experiments. These cells can improve polarized neutronic performance further by about 40 % compared to the current polarized MACS setup. These cells will employ a dedicated new cryostat with a smaller diameter tail, which is under construction. Concurrently, we are developing a polarized MACS capability that utilizes a CCR and a horseshoe cell to enable scientific applications for soft matter.

In a traditional polarized neutron reflectometer with a single incident wavelength, a supermirror is used for polarization analysis of specular reflection, whereas a $^3$He spin analyzer is needed for diffuse reflection. However, the simultaneous use of several wavelengths and multi-scattered beams in the CANDOR instrument requires a $^3$He spin analyzer for all experiments. We have collaborated with the CANDOR instrument responsibilities and engineering team on a conceptual design of the $^3$He spin analyzer. In phase I, we will operate with traditional, remotely polarized $^3$He cells to establish the polarized beam capability. An in-situ analyzer is under development for future experiments. We have also developed a polarized neutron capability using a superconducting magnet that allows for polarized beam experiments on BT-7 at sample magnetic fields up to 2 T, opening up many new scientific opportunities.
2016 ACCOMPLISHMENTS AND OPPORTUNITIES

FACILITY DEVELOPMENT

Data Acquisition Software

The New Instrument Control Environment (NICE) is a Java-based data acquisition package that incorporates a highly versatile scripting capability to enable end user adaptations to be coded under all the major scientific programming languages. This year, the graphical user interface (GUI) for SANS was completely overhauled. Its favorable user reviews spurred deployment at the NGB 30 m SANS, and now NICE has been deployed for full-time use on all three of the SANS instruments. This brings the total number of NCNR instruments controlled by NICE to eight. A special, polarized beam GUI has recently been tested on NG7 SANS, with good feedback. For vSANS, NICE is currently in testing, running with the existing hardware and incorporating new hardware as it is added. For CANDOR, gathering of software requirements is nearly complete.

Data Analysis Software

During the past year, many improvements have been made to the Data Analysis and Visualization Environment (DAVE) software package. The DAVE suite is the primary software package used on many of the neutron inelastic instruments at the NCNR for experiment planning, data visualization, reduction and analysis. A long overdue infrastructure overhaul was made when the entire source code was migrated from CVS on SourceForge, where it has resided for more than a decade, to an internal NIST repository running Git. This change was essential for reliability and better version control and management of the code repository for current and future developers. Besides the usual maintenance work that is necessary for a project of this maturity, there were new functionality and updates made in the areas of data reduction and analysis. To enhance usability, we have been gradually coalescing on two common interfaces for the data reduction modules representing each of the supported instruments in DAVE. This year it was the turn of the HFBS instrument; the data reduction modules covering dynamic and fixed window scan analysis were updated and new features added based on user requests. The new program modules provide an enriched user interaction experience and facilitate visual comparing and contrasting of multiple datasets. Built-in functions for momentum distribution analysis and a parametric empirical baseline function have been added to PAN. In addition, basic algebraic operations can now be applied to the fitted parameters making it straightforward to represent the results in ways that are more informative or amenable to further analysis.

Version 4.0 of the SASView data analysis program has been released. This release has a completely new modeling interface, making it easier for researchers to add their own models and share models with others. Models can be created using python or using C. In either case, features such as polydispersity on shape parameters are automatically available. Calculations can also take advantage of the extra computing capabilities on the CPU or on the graphics card to calculate patterns more quickly, often realizing several orders of magnitude speed improvement over SASView 3.1.

Reductus is the new reduction software for the NCNR reflectometers. Being web-based, the latest version of this software is automatically available to all users. The program links to the publicly available data from the NCNR, making it easy to retrieve and examine files. Reduction templates can be saved and shared, complete with all the parameters set by the user, completely capturing data provenance. All stages of the data reduction are visible, with the output available at each step, so problems in the final reduced data can be traced back to the step where they appear.

Funded jointly by the NSF and EPSRC, the CCP-SAS project is focused on developing an easy-to-use open-source modeling package that enables users to generate physically accurate atomistic models, calculate scattering profiles and compare results to experimental scattering data sets in a single web-based software suite. SASSIE-web is now available to the international scattering community. Several workshop and training sessions have taken place at scattering centers and scientific meetings. To date, over thirty-seven manuscripts using our software products on a variety of structural biology and soft-matter problems have been published. With hundreds of users the goals of the next year are to enable the software to utilize high performance computational methods to model scattering data.

FIGURE 5: A recently developed, compact $^3\text{He}$ polarizer with an integrated adiabatic fast passage NMR-based neutron spin flipper. The $^3\text{He}$ polarization flipping efficiency has been determined to be $3 \times 10^{-4}$ per flip.
The mission of the NIST Center for Neutron Research is to assure the availability of neutron measurement capabilities to meet the needs of U.S. researchers from industry, academia and other U.S. government agencies. To carry out this mission, the NCNR uses several different mechanisms to work with participants from outside NIST, including a competitive proposal process, instrument partnerships, and collaborative research with NIST.

Proposal System

Most of the beam time on NCNR instruments is made available through a competitive, peer-review proposal process. The NCNR issues calls for proposals approximately twice a year. Proposals are reviewed at several different levels. First, expert external referees evaluate each proposal on merit and provide us with written comments and ratings. This is a very thorough process where several different referees review each proposal. Second, the proposals are evaluated on technical feasibility and safety by NCNR staff. Third, we convene our Beam Time Allocation Committee (BTAC) to assess the reviews and to allocate the available instrument time. Using the results of the external peer review and their own judgment, the BTAC makes recommendations to the NCNR Director on the amount of beam time to allocate to each approved experiment. Approved experiments are scheduled by NCNR staff members in consultation with the experimenters.

The current BTAC members are:

- Andrew Allen (NIST Ceramics Division)
- Jeffrey Allen (Michigan Technological University)
- Collin Broholm (The Johns Hopkins University)
- Leslie Butler (Louisiana State University)
- Thomas Epps (University of Delaware)
- Kushol Gupta (University of Pennsylvania)
- Valery Kiryukhin (Rutgers University)
- Ramanan Krishnamoorti (University of Houston)
- Jennifer Lee (National Institutes of Health)
- Raul Lobo (University of Delaware)
- Janna Maranas (The Pennsylvania State University)
- Steven May (Drexel University)
- Lilo Pozzo (University of Washington)
- Stephan Rosenkranz (Argonne National Laboratory)
- Gila Stein (University of Houston)
- Stephen Wilson (University of California Santa Barbara)

Partnerships

The NCNR may form partnerships with other institutions to fund the development and operation of selected instruments. These partnerships, or “Participating Research Teams”, may have access to as much as 75% of the available beam time on the instrument, depending on the share of total costs borne by the team. A minimum of 25% of the available beam time is always made available through the NCNR proposal program to all users. Partnerships are negotiated for a fixed period (usually three years) and may be renewed if there is mutual interest and a continued need. These partnerships have proven to be an important and effective way to expand the research community’s access to NCNR capabilities.

Collaboration with NIST

Some time on all instruments is available to NIST staff in support of our mission. This time is used to work on NIST research needs, instrument development, and promoting the widespread use of neutron measurements in important research areas, particularly by new users. As a result of these objectives, a significant fraction of the time available to NIST staff is used collaboratively by external users, who often take the lead in the research. Access through such collaborations is managed through written beam time requests. In contrast to proposals, beam time requests are reviewed and approved internally by NCNR staff. We encourage users interested in exploring collaborative research opportunities to contact an appropriate NCNR staff member.

Research Participation and Productivity

The NCNR continued its strong record of serving the U.S. research community this year. Over the 2016 reporting year, 2536 research participants benefited from use of the NCNR. (Research participants include users who come to the NCNR to use the facility as well as active collaborators, including co-proposers of approved experiments, and co-authors of publications resulting from work performed at the NCNR.) As the number of participants has grown, the number of publications per year has increased in proportion.
2016 NCNR Proposal Program

In response to the last two calls for proposals (calls 33 and 34) for instrument time, we received 708 proposals, of which 405 were approved and received beam time. For the most recent call, the oversubscription, i.e., the ratio of days requested on all proposals to the days available, was 2.0 on average. Proposal demand has grown constantly since the NCNR first began accepting proposals in 1991, and has more than doubled in the past decade. The following table shows the data for several instrument classes.

<table>
<thead>
<tr>
<th>Instrument class</th>
<th>Proposals</th>
<th>Days requested</th>
<th>Days allocated</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANS and USANS</td>
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<td>892</td>
<td>476</td>
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<tr>
<td>Reflectometers</td>
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<td>673</td>
<td>360</td>
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<td>Spectrometers</td>
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<td>80</td>
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<tr>
<td>Total</td>
<td>708</td>
<td>3819</td>
<td>1863</td>
</tr>
</tbody>
</table>

Users Group

The NCNR Users Group (NUG) provides an independent forum for all facility users to raise issues to NCNR management, working through its executive officers to carry out this function. The current members of the NUG Executive Committee are Alan Nakatani (Dow Chemical, chair), Michael Crawford (University of Delaware), Amber Larson (University of Maryland, student/postdoc member), Michael Mackay (University of Delaware), Megan Robertson (University of Houston), Rafael Verduzco (Rice University) and Igor Zaliznyak (Brookhaven National Laboratory).

The NUG conducted a user survey in the fall of 2015. There were more than 450 responses the majority of whom are CHRNS users. Overall the results are encouraging with 5 of the 6 general categories

Panel of Assessment

The major organizational components of NIST are evaluated annually for quality and effectiveness by the National Research Council (NRC), the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering. A panel appointed by the NRC convened at the NCNR on July 7-8, 2015. Their findings are summarized in a published report, “An Assessment of the National Institute of Standards and Technology Center for Neutron Research: Fiscal Year 2015,” which is available at https://www.nap.edu/catalog/21878/an-assessment-of-the-national-institute-of-standards-and-technology-center-for-neutron-research. The panel members included Peter Green (University of Michigan, chair), Frank Bates (University of Minnesota), Bruce Gaulin (McMaster University), Janos Kirz (Lawrence Berkeley National Laboratory), V. Adrian Parsegian (University of Massachusetts Amherst), Sunhil Sinha (University of California at San Diego). A new panel is expected to convene at the NCNR in 2018.

The Center for High Resolution Neutron Scattering (CHRNS)

CHRNS is a national user facility that is jointly funded by the National Science Foundation and the NCNR. Its primary goal is to maximize access to state-of-the-art neutron scattering instrumentation for the research community. It operates five neutron scattering instruments at the NCNR, enabling users from around the nation to observe dynamical phenomena involving energies from \( \approx 30 \) neV to \( \approx 10 \) meV, and to obtain structural information on length scales from \( \approx 1 \) nm to \( \approx 10 \) µm. A more detailed account of CHRNS activities may be found on pp 61 of this report.

Partnerships for Specific Instruments

NG-7 SANS Consortium

A consortium that includes NIST, the ExxonMobil Research and Engineering Company, and the Industrial Partnership for Research in Interfacial and Materials Engineering (IPRIIME) led by the University of Minnesota, operates, maintains, and conducts research at the NG-7 30m SANS instrument. The consortium uses 57 % of the beam time on this instrument, with the remaining 43 % allocated to the general scientific community through the NCNR’s proposal system. Consortium members conduct independent research programs primarily in the area of large-scale structure in soft matter. For example, ExxonMobil has used this instrument to deepen their understanding of the underlying nature of ExxonMobil’s products and processes, especially in the fields of polymers, complex fluids, and petroleum mixtures.
The nSoft Consortium

Formed in August 2012, the nSoft Consortium allows member companies to participate with NIST in the development of advanced measurements of materials and manufacturing processes, and develop their own expertise in state-of-the-art measurement technologies to include in their analytical research programs. nSoft develops new neutron-based measurement science for manufacturers of soft materials including plastics, composites, protein solutions, surfactants, and colloidal fluids. Members receive access to leading expertise and training support in neutron technology and soft materials science at NIST. Contact: Ron Jones, nSoft Director, rljones@nist.gov, 301-975-4624.

NIST / General Motors – Neutron Imaging

An ongoing partnership and collaboration between General Motors and NIST, which also includes Honda Motors through GM’s partnership with Honda, continues to yield exciting results using neutron imaging. Neutron imaging has been employed to visualize the operation of fuel cells for automotive vehicle applications. Neutron imaging is an ideal method for visualizing hydrogen, the fuel of electric vehicle engines. These unique, fundamental measurements provide valuable material characterizations that will help improve the performance, increase the reliability, and reduce the time to market introduction of the next generation electric car engines. 25 % of the time on the BT-2 Neutron Imaging Facility is made available to the general scientific community through peer-reviewed proposals.

Interagency Collaborations

The Smithsonian Institution’s Nuclear Laboratory for Archaeological Research is part of the Anthropology Department at the National Museum of Natural History. It has had a longstanding and productive partnership with the NCNR, during which time it has chemically analyzed over 43,100 archaeological artifacts by Instrumental Neutron Activation Analysis (INAA), drawing extensively on the collections of the Smithsonian, as well as on those of many other institutions in this country and abroad. Such chemical analyses provide a means of linking these diverse collections together in order to study continuity and change involved in the production of ceramic and other artifacts.

The Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration (FDA), maintains laboratory facilities at the NCNR providing agency-wide analytical support for food safety and food defense programs. Neutron activation and low-level gamma-ray detection techniques yield multi-element and radiological information about foods and related materials and provide a metrological foundation for FDA’s field investigations and for radiological emergency response planning.
The Center for High Resolution Neutron Scattering (CHRNS)

The Center for High Resolution Neutron Scattering is a national user facility that is jointly funded by the National Science Foundation through its Division of Materials Research (grant number DMR-1508249) and by the NCNR. The core mission of CHRNS is fourfold: (i) to develop and operate neutron scattering instrumentation, with broad application in materials research, for use by the general scientific community; (ii) to promote the effective use of the CHRNS instruments by having an identifiable staff whose primary function is to assist users; (iii) to conduct research that advances the capabilities and utilization of CHRNS facilities; and (iv) to contribute to the development of human resources through educational and outreach efforts. The purpose of this partnership is to maximize access to state-of-the-art neutron scattering instrumentation for the academic research community using the NCNR’s proposal system. Proposals to use the CHRNS instruments are critically reviewed on the basis of scientific merit and/or technological importance.

Following the submission of a new proposal to NSF and a site visit in January 2015, the CHRNS agreement was renewed for five years beginning on September 1, 2015. The success of the proposal was based on CHRNS’s demonstrated ability to advance neutron scattering measurement capabilities and its prominent role in expanding, educating, and diversifying the community of researchers who use neutron methods. As part of the new agreement, the portfolio of instruments supported by CHRNS will continue to evolve to ensure that the scientific capabilities exceed or are comparable to the best worldwide. Input for these new directions was obtained from the scientific community through a variety of mechanisms including a user survey administered by the NCNR User Group (NUG) in the fall of 2015.

Scattering Instruments

During FY 2016, CHRNS supported operation of the following instruments: the NG-B 30 m Small Angle Neutron Scattering (SANS) instrument, the Ultra-Small Angle Neutron Scattering (USANS) instrument, the Multi-Angle Crystal Spectrometer (MACS), the High Flux Backscattering Spectrometer (HFBS), and the Neutron Spin-Echo (NSE) spectrometer. Combined, CHRNS instruments can provide structural information on a length scale of ≈ 1 nm to ≈ 10 µm, and dynamical information on energy scales from ≈ 30 neV to ≈ 10 meV. The CHRNS agreement continues programs in instrument operations and development on HFBS, NSE, and MACS, which boasts the world’s highest monochromatic cold-neutron flux and is now the premier instrument in the world for investigations of quantum magnetism. As part of the CHRNS agreement, two innovative instruments, vSANS and CANDOR, will be folded into CHRNS as the installation and commissioning of these new instruments progress. The data rates provided by the multiplex detector assembly of the CANDOR reflectometer will exceed those available elsewhere in the world by perhaps an order of magnitude. The versatile vSANS instrument will cover extensive nano-to-meso length scales in a single measurement, eliminating the need for combined experiments on uSANS and SANS in many cases. uSANS and SANS will thus be phased out of CHRNS following the commissioning of vSANS and CANDOR.

Research

The wide ranges of instrument capabilities available in CHRNS support a very diverse scientific program, allowing researchers in materials science, chemistry, biology, and condensed matter...
physics to investigate materials such as polymers, metals, ceramics, magnetic materials, porous media, fluids and gels, rock formations, and biological molecules.

In the most recent Call for Proposals (call 34), 197 proposals requested CHRNS instruments, and 109 of these proposals received beam time. Of the 967 days requested for the CHRNS instruments, 503 were awarded. Roughly half of the users of neutron scattering techniques at the NCNR use CHRNS-funded instruments, and approximately one third of NCNR publications (see the “Publications” section on p. 67), over the current one-year period, are based on research performed using these instruments. This report contains several highlights of these CHRNS publications. See the labeled highlights in the table of contents.

**Scientific Support Services**

In FY 2016, CHRNS provided scientific support in three critical areas: sample environment, chemical laboratories, and the production and delivery of polarized neutron beams. The laboratory staff continues to equip and maintain user laboratories and routinely assists users with sample preparations. The staff also ensures that users have the tools and supplies they need for a successful experiment.

The CHRNS Sample Environment team provides users with the equipment and training needed to make neutron measurements under external conditions of temperature, pressure, magnetic field, humidity, and fluid flow. Two new Peltier blocks, which will allow for more efficient temperature changes in routine SANS experiments, are currently in the commissioning stages. In addition, a new heat shield extension and vacuum shroud extension were added to the HFBS closed-cycle refrigerator enabling temperatures of 800 K at the sample position.

As a result of the CHRNS support for the NCNR effort in $^3$He spin filters, full polarized beam capabilities are available to users of the MACS and SANS instruments within the CHRNS suite. Currently, both instruments make frequent use of record-breaking $^3$He spin analyzer cells with specialized geometries. It is also notable that CHRNS runs the only SANS program in the U.S. that routinely operates with full polarization analysis, and MACS provides the most intense polarized cold neutron beam with the largest scattering angle coverage for polarization analysis. From August 2015 through July 2016, the $^3$He Spin Filter team serviced 13 user experiments on the CHRNS instruments MACS and SANS. In the future, both the vSANS instrument and CANDOR will produce spin-polarized incident beams using a double-V supermirror polarizer (efficiency of > 95 %), along with an RF spin flipper (efficiency of 99.5 %), and will be spin-analyzed by a $^3$He spin filter.

**Education and Outreach**

This year the Center for High Resolution Neutron Scattering sponsored a variety of educational programs and activities tailored to specific age groups and professions. The twenty-second annual summer school, held on June 27 – July 1, 2016 was entitled “Methods and Applications of Small Angle Neutron Scattering and Neutron Reflectivity.” Forty graduate and postdoctoral students from 27 universities participated in the school. Lectures, research seminars and were highlighted for a wide variety of neutron measurement techniques. The guest lecturers were Prof. Michael Hore from Case Western University, Prof. Steve May from Drexel University, and Dr. Marilia Cabral from the Memorial Sloan Kettering Cancer Center. The evaluations were excellent and student feedback was very positive.
As part of its expanding education and outreach effort, CHRNS offers the opportunity to request travel support for an additional graduate student to participate in the experiment to university-based research groups with BTAC-approved experiment proposals. This support is intended to enable new graduate students, for example, to acquire first-hand experience with a technique that they may later use in their own research. Announcements of this program are sent to all of the university groups whose experiment proposals receive beam time from the BTAC. Recipients of the announcement are encouraged to consider graduate students from under-represented groups for this opportunity. The program is also advertised on the NCNR’s website at http://www.ncnr.nist.gov/outreach.html.

As in previous years, CHRNS participated in NIST’s Summer Undergraduate Research Fellowship (SURF) program. In 2016, CHRNS hosted 14 SURF students, including two returning SURF interns from the previous year and two previous participants in the SHIP program. The students participated in research projects such as selective gas adsorption in metal organic frameworks, characterization of nanoparticle architecture in composite polymers, optimization of the cold neutron source design for a proposed new research reactor, and refining a Markov Chain Monte Carlo algorithm for fitting reflectometry data. They presented their work at the NIST SURF colloquium in early August 2016 in sessions moderated by programming officers from the National Science Foundation.

The annual Summer Institute for Middle School Science Teachers brings middle school science teachers from across the United States to NIST for two weeks in order to give them a better understanding of the scientific process. Each year, CHRNS hosts the teachers for a one-day introduction to neutron scattering with a presentation that describes how neutrons are produced and how they are used to improve our understanding of materials at the atomic scale. This year the Summer Institute hosted twenty-four teachers from five states, including South Dakota and California. On July 19th, the teachers learned about the types of experiments performed using neutron methods after having toured the neutron guide hall and seeing several neutron instruments. To bring home projects suitable for middle school students, they then learned how to grow crystals of “alum” (hydrated aluminum potassium sulfate). Throughout the day and at lunchtime, the teachers had the opportunity to interact with staff members.

A large number of specialized tours for middle school, high school, and university students were also offered throughout the year.
The 2016 Clifford G. Shull Prize from the Neutron Scattering Society of America has been awarded to the NCNR’s Chuck Majkrzak. The award was presented at the 8th American Conference on Neutron Scattering held in July 2016. Chuck is recognized “For leadership in the development, application, and establishment of neutron reflectivity as an essential measurement tool for nanoscale materials.”

The NCNR’s Yun Liu was awarded the 2016 Science Prize by the Neutron Scattering Society of America, presented at the 8th American Conference on Neutron Scattering. The citation reads: “For the discovery of dynamic cluster ordering in complex colloidal and protein systems using neutron scattering.” The NSSA Science Prize recognizes a major scientific accomplishment or important scientific contribution within the last 5 years using neutron scattering techniques.

Craig Brown of the NCNR, along with Jeff Long of UC Berkeley, received the 2016 Hydrogen Storage Award from DOE’s Hydrogen and Fuel Cells Program. This award recognizes Craig and Prof. Long for their “decades of dedication and achievements in adsorbent-based hydrogen storage materials development and characterization. Craig used neutron diffraction experiments to characterize and subsequently confirm the results, which offer a pathway for significantly improved hydrogen storage capacity for adsorbent-based hydrogen storage materials.”

P. Douglas Godfrin, University of Delaware, is the recipient of the 2016 Prize for Outstanding Student Research of the Neutron Scattering Society of America (NSSA) with the citation: “For seminal neutron scattering studies of concentrated protein solutions and protein dynamics with application to biopharmaceutical engineering.”

NCNR’s Nick Butch received the 2016 Katharine B. Gebbie Young Investigator Award presented by the NIST chapter of Sigma Xi. Nick is being recognized for “seminal contributions to the study of unconventional superconductors, topological insulators, and other quantum matter.”

Dennis Nester of the NCNR received the 2015 NIST Colleagues’ Choice Award. The Colleagues’ Choice Award honors the outstanding achievements and contributions made by selected individuals in support of the NIST mission as determined by their colleagues. Dennis is being recognized “For dedicated support of safe and reliable NCNR cold neutron source operation and invaluable assistance to hundreds of NIST staff and visitors.”

The NCNR’s Joseph Curtis was selected by the Secretary of Commerce to receive the Silver Medal. Joseph is being recognized “For developing and making globally available the SASSIE software suite used to model complex biological molecules from small-angle scattering data.”

Doug Ogg, Jim Moyer, and Mike Rinehart of the NCNR received the Department of Commerce Bronze Medal Award for their work on the MACS detector/analyzer installation. The specific citation for the award is “For the mechanical design, installation, and alignment of a complex neutron analyzer and detection system on the NCNR Multi-Axis Crystal Spectrometer.”
2016 Accomplishments and Opportunities

NCNR’s Liz Kelley received the Most Outstanding Poster Award in the area of Biology/Biotechnology for her poster entitled “Towards understanding the role of lipid diversity in tuning biomembrane dynamics” at the annual Sigma Xi Post-doc poster presentation.

Michelle Jamer of the NCNR won the Best Poster prize at the Gordon Research Conference on Multiferroics and Magnetoellectric Materials in Lewiston, Maine. She won the award for her poster titled “Probing the depth dependent magnetization of FeGa/NiFe multilayers using polarized neutron reflectometry.”

John R. D. Copley of the NCNR has been named a 2016 NSSA Fellow “For outstanding research on the physics of liquids and fullerenes and major contributions to neutron instrument development and scattering data analysis.”

Michelle Calabrese of the University of Delaware received a student poster award at the American Conference on Neutron Scattering in July. Her poster was titled “Using spatiotemporal small angle neutron scattering to determine the effect of micellar branching on non-linear shear flow phenomena and instabilities.”

Jacob LaManna of the Neutron Physics Group was named runner-up in the category of Physics/Engineering at the annual Sigma Xi Post-doc poster presentation for his poster “Simultaneous multimodal neutron and X-ray imaging for multiphase quantifications in engineering and material science.”

Julie Borchers has been recognized for Outstanding Service to the Neutron Scattering Society of America. Julie served on the NSSA Executive Committee as Secretary from 1999-2002 and most recently as Vice-President from 2010-2014.

Dan Hussey of the Neutron Physics Group was awarded the Arthur S. Flemming Award for his pioneering work in neutron imaging. The Flemming Awards, which were established by the Downtown Jaycees in 1948, honor outstanding federal employees with 3 to 15 years of federal service for their exceptional contributions to the federal government.

Thomas H. Epps, III from the University of Delaware has been awarded the 2016 John H. Dillon Medal from the American Physical Society “for significant advancement in the control, characterization, and understanding of polymer nanoscale-structure and energetics” Epps is the Thomas and Kipp Gutshall Associate Professor of Chemical and Biomolecular Engineering and Associate Professor of Materials Science and Engineering at the University of Delaware, and is a frequent user of the NCNR.

Matthew E. Helgeson, Assistant Professor of Chemical Engineering at the University of California at Santa Barbara, has been awarded the Unilever Award by the American Chemical Society at their 90th ACS Colloid & Surface Science Symposium. The award is given in recognition of fundamental work in colloid or surfactant science carried out in North America by researchers in the early stages of their careers. Matt’s research is devoted to the design and processing of complex fluids and colloidal soft matter with well-specified mesostructure, and he makes frequent use of small angle scattering facilities at the NCNR.

Prof. Kate Ross was awarded the American Physical Society’s 2016 Valley Prize “for the elucidation of quantum frustrated magnetism and its expression in the ground state selection of pyrochlore magnets.” The biennial prize recognizes “one individual in the early stages of his or her career for an outstanding scientific contribution to physics that is deemed to have significant potential for a dramatic impact on the field.” Kate was a recent post-doc at the NCNR and Johns Hopkins.

The European Colloid and Interface Society has awarded Prof. Piero Baglioni the 2016 Overbeek Gold Medal in recognition of his outstanding contributions to colloid and interface science. Piero is a Professor of Physical Chemistry at the University of Florence, and is a long time user of the NCNR and collaborator with NCNR staff.
Prof. Norman Wagner has been inducted as a fellow into the National Academy of Inventors, in ceremonies at the United States Patent and Trademark Office in Alexandria, Virginia. Wagner, who is the Unidel Robert Pigford Chaired Professor of Chemical and Biomolecular Engineering at the University of Delaware, has developed “super-hero” materials called shear-thickening fluids – some that he has developed into “liquid armor”, and studying these fluids using neutrons at the NCNR.

Mircea Dincă, Professor of Chemistry at MIT, has been selected by the NSF as the 2016 Alan T. Waterman Award winner. The award citation (in part) notes “Mircea’s research has demonstrated that metal organic frameworks (MOF) can store electrical energy – something previously unknown, and his research in microporous solids is revolutionizing how scientists approach this exciting new technology, opening the door for future discoveries.” He is a frequent user of the NCNR.

Prof. Pengcheng Dai of Rice University is the recipient of the 2016 Sustained Research Prize of the Neutron Scattering Society of America (NSSA) Prof. Dai is a frequent user of the NCNR, and was cited for: “his sustained and foundational contributions which have elucidated the magnetic properties of iron-based superconductors, cuprates, and other correlated electron materials.”

Efrain E. Rodriguez, Assistant Professor of Chemistry and Biochemistry at the University of Maryland has been selected as an Emerging Investigator by the Journal of Materials Chemistry C (Royal Society of Chemistry). He was recognized for “carrying out work with the potential to influence future directions in materials chemistry.” His research areas include iron-based superconductors, magnetic materials, transition metal oxides, crystallography, and make use of neutron scattering at the NCNR.

Two UMD graduate students working with Efrain Rodriguez received 2016 Margaret C. Etter Student Lecturer Awards at the recent meeting of the American Crystallographic Association. Amber Larson, who serves on the NCNR User Group Executive Committee, won in the area of Neutron Scattering for her presentation entitled “Complex magnetism and metal-insulator transitions in Hollandite transition-metal oxides.” Daniel Taylor won in the area of Powder Diffraction for his talk entitled “Oxygen storage properties of La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ for chemical-looping reactions.” Daniel was also awarded a 2016 Ludo Frevel Crystallography Scholarship from the International Centre for Diffraction Data for his thesis: “Reactivity and Oxygen Storage in Materials for Chemical Looping Processes.”


Yang, J., Duan, C., Copley, J.R.D., Brown, C.M., Louca, D., “The Magnetic Transitions and Dynamics in the Multiferroic Lu$_{0.5}$Sc$_{0.5}$FeO$_3$,” in “MRS advances,” edited by Oyen, M.L., (MRS Advances, October 2015, Boston, MA) 1, 565 (2016).


Instruments and Contacts

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High resolution powder diffractometer (BT-1):
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• Q. Z. Huang, 6164, qing.huang@nist.gov
• C. M. Brown, 5134, craig.brown@nist.gov

Residual stress diffractometer (BT-8):
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30-m SANS instrument (NG-7):
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30-m SANS instrument (NG-B 30m) (CHRNS):
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• C. Gagnon, 2020, cedric.gagnon@nist.gov

10-m SANS instrument (NG-B) (nSoft):
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• K. Weigandt, 8396, kathleen.weigandt@nist.gov

USANS, Perfect Crystal SANS (BT-5) (CHRNS):
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• P. D. Butler, 2028, paul.butler@nist.gov

Polarized Beam Reflectometer/Diffractometer (NG-D):
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MAGIK, Off-Specular Reflectometer (NG-D):
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Neutron reflectometer-horizontal sample (NG-7):
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Double-focusing triple-axis Spectrometer (BT-7):
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SPINS, Spin-polarized triple-axis spectrometer (NG-5):
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Triple-axis spectrometer (BT-4):
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FANS, Filter-analyzer neutron spectrometer (BT-4):
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DCS, Disk-chopper time-of-flight spectrometer (NG-4):
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HFBS, High-flux backscattering spectrometer (NG-2) (CHRNS):
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NSE, Neutron spin echo spectrometer (NG-A) (CHRNS):
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MACS, Multi-angle crystal spectrometer (BT-9) (CHRNS):
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Cold-neutron prompt-gamma neutron activation analysis (NG-D):
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Thermal-neutron prompt-gamma activation analysis (VT-5):
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Other activation analysis facilities:
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Cold neutron depth profiling (NG-1):
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Neutron interferometer (NG-7):
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Fundamental neutron physics station (NG-C):
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CANDOR, White-beam reflectometer/diffractometer:
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Copies of annual reports, facility information, user information, and research proposal guidelines are available electronically.

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