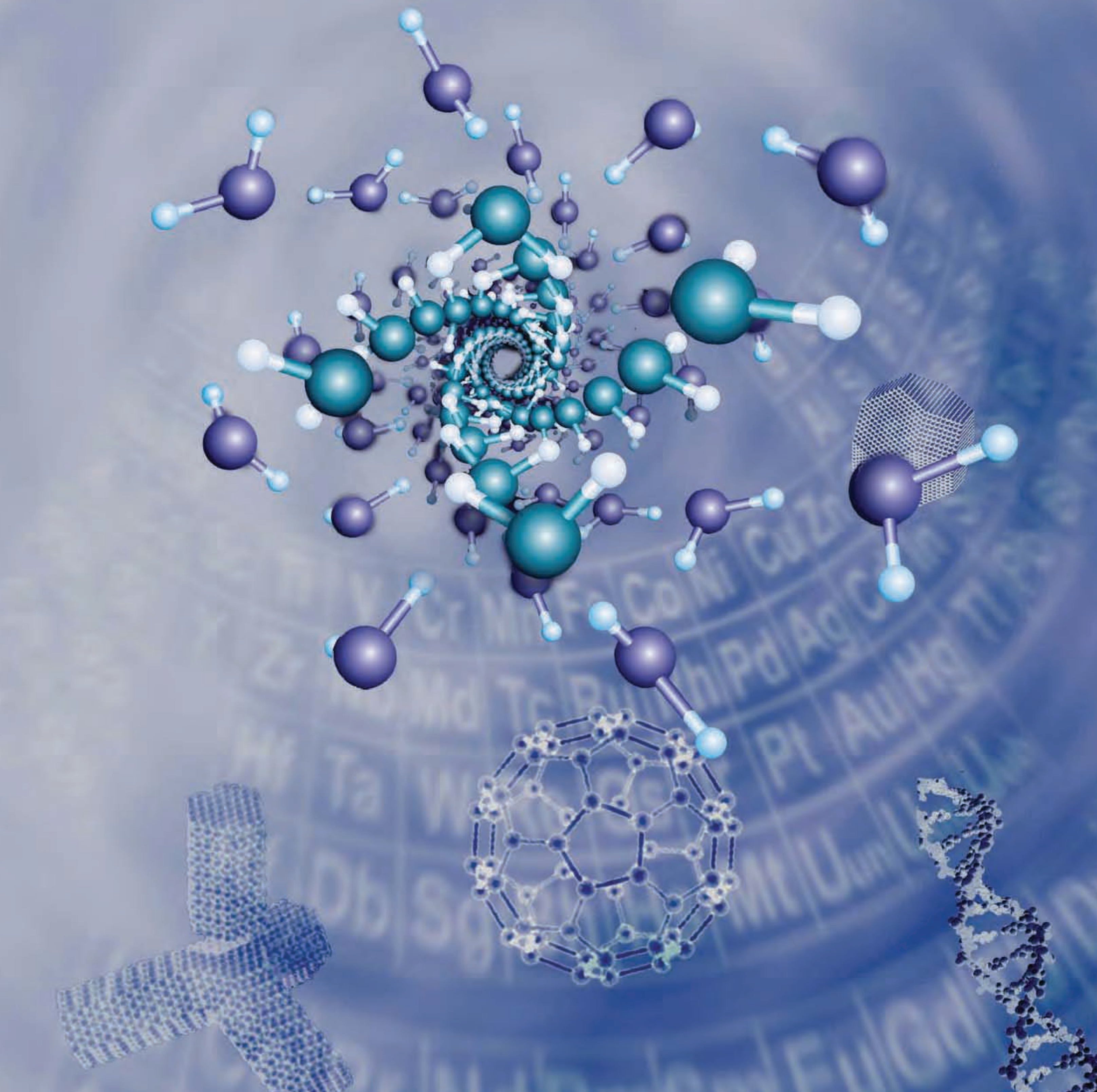
X-RAYS AND NEUTRONS

Essential Tools for Nanoscience Research

Report of the National Nanotechnology Initiative Workshop
June 16-18, 2005



About the National Nanotechnology Initiative

The National Nanotechnology Initiative (NNI) is a coordinated Federal research and development program that brings together the expertise from twenty-five Federal agencies to guide and support advancement across the field of nanotechnology. The vision of the NNI is a future in which the ability to understand and control matter at the nanoscale leads to a revolution in technology and industry that benefits society. NNI agencies share goals, priorities, and strategies toward achieving this vision. The initiative is coordinated through the Nanoscale Science, Engineering, and Technology (NSET) Subcommittee of the Committee on Technology, National Science and Technology Council, with the administrative and technical support of the National Nanotechnology Coordination Office (NNCO).

For more information on the NNI, the NSET Subcommittee, and the NNCO, see www.nano.gov.

About this document

This document is the report of a workshop held June 16-18, 2005 in Washington, DC. The workshop was organized by the U.S. Department of Energy, the National Science Foundation, and the National Institute of Standards and Technology, with assistance from the NNCO and the endorsement of the NSET Subcommittee. The workshop sought input from the research community on the use of x-ray and neutron techniques to advance nanoscale science, engineering, and technology. The workshop and this report are intended to further the research agenda of the sponsoring agencies and fulfill the goals of the National Nanotechnology Initiative by identifying research opportunities, stimulating interactions between academic, industrial, and government scientists, and identifying improvements to our national research infrastructure needed to best support research and development activities at the nanoscale in coming decades.

Cover and book design

Book design and layout by NNCO and Argonne National Laboratory staff members. Cover design by Nicolle Rager Fuller of Sayo-Art.

Front cover: When confined inside carbon nanotubes, water can self-assemble into nano-ice with a double helical structure similar to DNA. The helical form of nano-ice was discovered by Dr. Cheng Zeng of the University of Nebraska-Lincoln's (UNL), who used UNL's PraireFire supercomputer to perform molecular dynamics simulations over a wide range of temperatures and pressures. Oxygen atoms are depicted as blue in the inner helix, purple in the outer helix. Hydrogen atoms are depicted as white and light blue. (Courtesy of the National Academy of Sciences, *PNAS* 103:19664 (2006). doi:10.1073/pnas.0608401104)

Copyright information

Printed in the United States of America. 2008.

X-rays and Neutrons: Essential Tools for Nanoscience Research

Report of the National Nanotechnology Initiative Workshop
June 16-18, 2005, Washington, D.C.

Workshop Chairs

Ian S. Anderson
Oak Ridge National Laboratory

Linda Horton
Oak Ridge National Laboratory

Eric Isaacs
Argonne National Laboratory and University of Chicago

Mark A. Ratner
Northwestern University

Sponsored by

U. S. Department of Energy
Office of Basic Energy Sciences

National Institute of Standards and Technology
NIST Center for Neutron Research

National Science Foundation
Division of Materials Research

ACKNOWLEDGMENTS

The principal sponsors of this workshop were the U.S. Department of Energy, the National Science Foundation, and the National Institute of Standards and Technology. The sponsors gratefully acknowledge the contributions of the workshop organizers and session leaders, who are also the principal authors of this report. They also thank all workshop attendees for thoughtful presentations and for participating in the discussions that provide the scientific content and motivation for the report. Overall guidance for the workshop and report was provided by Kristin Bennett of the Office of Basic Energy Sciences, U.S. Department of Energy, and Philip Lippel of the National Nanotechnology Coordination Office. Thanks are also due to the National Science Foundation Divisions of Materials Research and Chemistry and the Joint Institute for Neutron Sciences for supporting the Early Career Poster Competition.

The efforts of the organizing committee and administrative staff were essential in the planning and execution of the workshop.

The sponsors wish to acknowledge special administrative assistance from:

Linda Cerrone, U.S. Department of Energy, Office of Basic Energy Sciences
Karen Talamini, U.S. Department of Energy, Office of Basic Energy Sciences
Athena Jones, National Science Foundation (intern), Division of Materials Research
Victor Turner, National Nanotechnology Coordination Office

and the efforts of the organizing committee:

Patrick Gallagher, National Institute of Standards and Technology, Center for Neutron Research
Stephen Gould, National Nanotechnology Coordination Office
Geoff Holdridge, National Nanotechnology Coordination Office
Allen Ekkebus, Oak Ridge National Laboratory, Spallation Neutron Source
Helen Kerch, U.S. Department of Energy, Office of Basic Energy Sciences
Celia Merzbacher, Office of Science and Technology Policy
Guebre X. Tessema, National Science Foundation, Division of Materials Research

The workshop chairs would like to acknowledge writing and editorial assistance from Charlie Horak and the graphic illustration contributions from Renee Manning, both from the Spallation Neutron Source at Oak Ridge National Laboratory. The chairs would also like to acknowledge editorial and production assistance from Derrick Mancini from the Center for Nanoscale Materials; Richard Fenner and Marlene Nowotarski from the Advanced Photon Source; and Lorenza Salinas and Vicki Skonicki from the Technical Services Division, all at Argonne National Laboratory, and from Jacqueline Ruttimann for WTEC.

Finally, the sponsors would like to thank the members of the National Science and Technology Council's Subcommittee on Nanoscale Science, Engineering, and Technology for endorsing the workshop.

This workshop was sponsored by the U.S. Department of Energy, the National Science Foundation, and the National Institute of Standards and Technology, and endorsed by the National Science and Technology Council's Subcommittee on Nanoscale Science, Engineering, and Technology. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the United States Government or the authors' parent institutions.

PREFACE

In order to advance knowledge and improve understanding in the fields of nanoscale science, engineering, and technology, and to promote their application for the benefit of the nation, the Government of the United States supports an interdisciplinary program in nanoscience, nanoengineering, and nanotechnology coordinated across several agencies. The President's 2006 budget provided over $1 billion for this multidisciplinary National Nanotechnology Initiative (NNI). The goals of the NNI are as follows:

- advance a world-class nanotechnology research and development (R&D) program
- foster the transfer of new technologies into products for commercial and public benefit
- develop and sustain educational resources, a skilled workforce, and the supporting research infrastructure and tools to advance nanotechnology
- support responsible development of nanotechnology

This document, reporting on the NNI workshop *X-rays and Neutrons: Essential Tools for Nanoscience Research*, attempts to help the NNI community meet these goals, especially by contributing to the multiagency effort to strengthen the nation's infrastructure for nanoscience research. The concept for the workshop was developed by the meeting sponsors—the U.S. Department of Energy, the National Science Foundation, and the National Institute of Standards and Technology, in consultation with all members of the Nanoscale Science, Engineering, and Technology Subcommittee of the National Science and Technology Council—to support long-range planning efforts for the NNI.

Stimulated in part by an earlier NNI workshop, *Instrumentation and Metrology for Nanotechnology*, the sponsors identified a need to better articulate the relationship between ongoing U.S. efforts in x-ray and neutron science and the research and development activities of the National Nanotechnology Initiative. To meet this need, they organized a topical workshop in June 2005, bringing researchers together to discuss the current state of x-ray and neutron scattering centers and their associated instrumentation, planned future capabilities for these centers, and how to best use the outputs of x-ray and neutron R&D to advance nanoscale science, engineering, and technology. While the previous NNI workshop assessed basic instrumentation and metrology needs across all nanoscience and nanotechnology, its principal focus was on high resolution tools such as electron microscopes and scanned probe instruments that typically serve individual investigators laboratories or small groups. The present workshop complements that study by concentration on large-scale, accelerator-based x-ray and neutron facilities and their associated tools, which are typically operated as user facilities.

The workshop drew over 150 participants—many of them internationally renowned specialists from the nanotechnology, x-ray scattering, and neutron scattering communities—for two full days of meetings in a collaborative environment. Their deliberations and discussions are captured in this report, as compiled by the Workshop chairs.

One aim of the workshop and this report is to exchange information between the nanoscience, x-ray, and neutron communities regarding the breadth, power, and application of these scattering tools for nanoscale science, engineering, and technology. A second aim is to provide a roadmap for universities, researchers, industry, governmental agencies, and policy makers recommending tools and techniques that are especially worthy of development in the next 5, 10, and 20 years. A third aim is to make the broader scientific community aware of the opportunities to use the open-access—often free—x-ray and neutron user facilities in which the U.S. Federal Government has invested heavily over the past five decades. A fourth aim is to ensure the competitiveness of the United States in nanotechnology by leveraging the power of x-ray and neutron science in its research and development.

The report identifies seven crosscutting research target areas synthesized from the discussions held at the workshop. It documents worldwide resources and demonstrates the need for sustained U.S. investment in neutron and x-ray source generation, instrumentation, tools, and analysis. It outlines current opportunities and suitable future goals for neutron- and x-ray-based nanoscience. Finally, it presents and recommends a 20-year roadmap for the development of improved x-ray and neutron facilities.

The research target areas and roadmap represent the scientific communities' recommendations as to where x-ray and neutron scattering have the greatest potential for accelerating nanotechnology R&D, and thus for helping the NNI make significant contributions to society and to our national economy. As such, they provide useful recommendations to university, government, industry, and policy makers regarding future investments in the areas of x-ray, neutron, and nanoscale science, engineering, and technology.

On behalf of the NSET Subcommittee, we wish to thank Drs. Ian S. Anderson, Linda Horton, Eric Isaacs, and Mark Ratner for their creativity and hard work in conducting an outstanding workshop and in preparing this report. The support and encouragement of Dr. Mihail Roco of the National Science Foundation, Chair of the NSET Subcommittee at the time of the workshop, helped make the workshop a reality. We are grateful for his leadership, and thank him on behalf of the organizers and sponsors.

We also thank all the speakers, session chairs, and participants for taking the time and effort to attend the workshop and to make their individual contributions. Their insights and generous sharing of research results ensure that this document and the roadmap it proposes for the future of x-rays and neutrons in nanotechnology will serve as a valuable reference for the NNI.

E. Clayton Teague, Director
National Nanotechnology
Coordination Office

Altaf Carim, Co-Chair
Nanoscale Science,
Engineering, and Technology
Subcommittee

Celia Merzbacher, Co-Chair
Nanoscale Science,
Engineering, and
Technology Subcommittee

TABLE OF CONTENTS

EXECUTIVE SUMMARY

For more than 50 years, x-ray- and neutron-based tools have opened new vistas at the (often intersecting) frontiers of materials science, biology, medicine, physics, chemistry, engineering, and the geological sciences. X-rays and neutrons are superb real-time probes of matter, capable of revealing details of structure (position) and dynamics (motion) at the atomic scale. An extensive infrastructure has been developed, in the United States and internationally, allowing scientists and engineers to exploit these tools. Researchers travel to large-scale facilities situated around the globe where intense, brilliant sources of x-rays and neutrons serve as unique windows into the properties of liquids, solids, gases, and plasmas. Their investigations are increasingly relevant to the emerging, interdisciplinary field of nanotechnology[1]. New advanced characterization techniques, increasingly sophisticated optics for beam focusing, and improved detectors and data analyses are making today's x-ray and neutron sources unprecedented tools for exploring fundamental science, engineering, and technology at the nanometer scale.

Accelerator-based "light sources" and their associated instrumentation deliver exceptionally intense, tightly focused beams of x-rays (and also ultraviolet (UV) or infrared (IR) radiation). Reactor- and accelerator-based neutron sources produce powerful, highly penetrating, focused monochromatic or polychromatic beams. Both neutron and x-ray scattering facilities enable atomic- or molecular-level investigations of many different kinds of samples, allowing the characterization of matter in all its phases; engineering devices; biological systems; and micromachines or nanomachines. X-ray and neutron-based instrumentation and analysis techniques are often non-destructive, can be performed *in situ* (i.e., in special environments such as at high temperatures or pressures), and can fully probe the structure of three-dimensional samples. Future scattering facilities with even greater capabilities promise to be important discovery platforms supporting the goals of the National Nanotechnology Initiative (NNI).

In June 2005 over 150 leading experts came together for the NNI topical workshop *X-rays and Neutrons: Essential Tools for Nanoscience Research*. Their task was to help articulate the relationship between x-ray and neutron science and the research and development activities of the NNI. A particularly important charge was to analyze how new instruments, tools, and techniques, just now becoming feasible, could best be developed to maximize their utility at the nanoscale.

The meeting included morning plenary talks and afternoon breakout sessions over two full days. Findings from each afternoon session were compiled by the session chairs and then presented to the full conference group in summary sessions. A third half-day session allowed the breakout leaders and workshop chairs to organize the findings into cross-cutting research target areas and to discuss a road map for the future facilities, tools, and investigations.

X-rays were identified as being particularly important for: measuring structural parameters of individual and ensembles of nanoparticles, nanocomposites (including defects and strains), and macromolecules; determining elemental composition and bonding states at surfaces and interfaces; characterizing growth processes *in situ*; direct probing of catalytic activity; investigating the dynamics

---

[1] We generally use the word nanotechnology in this report in an inclusive manner, incorporating nanoscale science, engineering, and technology.

of protein folding, entangled polymers, and glassy materials; and studying ultrafast dynamics of chemical reactions and charge transfer processes in nanodevices.

Neutrons were identified as being especially useful for studying: nuclear and magnetic structure of thin films; structure of polymers, proteins, and nucleic acids at the nanometer length scale; structure and dynamics of adsorbed species, reaction intermediates, and chemical products on catalytic surfaces; dynamics of protons in hydrogen-bonded materials; and structure and spin dynamics of molecular magnets or assemblies of magnetic nanoparticles.

For both x-ray- and neutron-based techniques, the opportunity to perform experiments non-destructively under controlled environments simulating realistic processes, or under extreme conditions at which unusual phenomena occur, was seen as a particularly enabling capability for nanotechnology researchers.

Seven cross-cutting research target areas emerged from these discussions of the capabilities of x-ray- and neutron-based techniques:

- Dynamics: Lessons for Nanotechnology from Nature
- Nanomaterials: Understanding the Impact of the Real World
- Extreme Environments
- User-Friendly Modeling: The Nano Toolbox
- Nanoparticles: The Ultimate in Precision Metrics
- Next-Generation Electronics: Following a Single Spin
- Nanoprocessing and Nanomanufacturing

To maximize progress in these research target areas and throughout nanotechnology R&D, the workshop chairs mapped the targets to five suggested categories for investment in U.S. x-ray and neutron resources. Their roadmap recommends high-priority programs over 5-, 10-, and 20-year periods, in the following categories: Ultrafast Dynamics, Bridging from Nano to Macro, Single-Particle Characterization, Real Environments, Cyberinfrastructure, and Beyond the Next Ten Years.

1. Introduction

1.1 BACKGROUND ON X-RAY AND NEUTRON SCIENCE AND FACILITIES

The Power of X-rays and Neutrons

The fundamental nature of x-rays and neutrons provides us with unique and powerful windows into the structure and dynamics of almost all forms of matter at the nanoscale. X-rays and neutrons are superb probes for exploring the frontiers of nanoscience because they are sensitive to structural features with lengths from 10^{-3} to 10^{3} nm, and to dynamic properties with characteristic time scales from 10^{-16} to 10^{3} s for x-rays and from 10^{-18} to 10^{-6} s for neutrons. They are readily produced with wavelengths that are comparable to the atomic spacing in solids and liquids, and kinetic energies that are comparable to those of dynamic processes in materials.

By using focusing optics and moderation techniques to prepare beams of these particles with appropriate energies and then monitoring their interactions with matter, scientists can measure the arrangements of atoms (structure) and can track the movements of atoms or molecules (dynamics). Using energetic beams of x-rays or neutrons, atomic positions can be measured to subnanometer precision. The shape of an object or arrangement of atoms inside objects as large as several centimeters can be determined using diffraction, scattering, spectroscopy, or direct imaging methods. X-rays and neutrons can be used to study dynamics on time scales ranging from attoseconds to many seconds, helping to elucidate the nature of processes as fast as electron transfer and as slow as molecular diffusion.

X-rays as well as neutrons interact weakly with most materials, so both are nondestructive and penetrate deeply into samples. They are suitable for *in situ* studies of materials during processing and under real or extreme conditions of temperature, pressure, and magnetic or electric fields. Both probes are highly sensitive to the detailed three-dimensional magnetic structure of materials; they can be used to measure dynamics of electron transfer or of magnetic processes such as spin waves or domain reorientation. Yet these two probes also interact differently with materials. An x-ray photon interacts primarily with the electron cloud surrounding the atomic nucleus, while a neutron of similar wavelength interacts with the nucleus itself. Techniques which employ them can therefore be highly complementary. X-rays are less sensitive to light atoms, while neutrons are particularly sensitive to hydrogen (the lightest atom). X-rays lend themselves to high resolution imaging, such as structural studies of single particles, while neutrons excel at looking at the dynamics and structure of interacting assemblies of particles.

Scattering Facilities

To make the power of x-ray and neutron scattering available to researchers from industry, government laboratories, and academia, the international scientific community has made an enormous investment in and commitment to x-ray and neutron facilities infrastructure. Accelerator-based “light sources” make exceptionally intense, tightly focused beams of x-rays (as well as infrared (IR) and ultraviolet radiation (UV)) available for both basic science and applied technology research. Neutron reactors provide monochromatic beams of neutrons, while accelerator-based "spallation sources" provide highly intense, pulsed polychromatic beams of neutrons. In either case, additional equipment is needed to moderate, collimate, and focus the beam. The facilities consisting of these sources and their associated instrumentation and staff resources are important R&D tools across many disciplines of science, engineering, and technology.

A synchrotron consists of a source of electrons (or sometimes positrons) that are accelerated and injected into a storage ring, where they are further accelerated to energies between ~ 500 MeV and 8 GeV depending on the size of the ring. As the charged particles are bent around the ring (by sophisticated magnets or multipole magnetic devices), energy is dissipated but captured in the form of x-rays. These x-rays are highly intense, highly focused, and strongly polarized. They emerge with energies from 0.1 keV (corresponding to a wavelength of 12.4 nm, known as "soft" x-rays) to 100 keV (0.0124 nm "hard" x-rays), and are thus well suited to investigations at the nanoscale (~1-100 nm). Second and later generation x-ray synchrotrons [see Figure 1.1] use devices like undulators to sharply bend the electron (or positron) beam; their x-ray output may be ten orders of magnitude brighter than a conventional laboratory x-ray source. The intense x-rays generated in this way are captured into beamlines tangent to the orbit of the charged particles in the storage ring. They can be further tailored for scattering, imaging, or spectroscopy at experimental stations located at the end of these beamlines, and configured to optimize resolution, intensity, or throughput for *in situ* measurements.

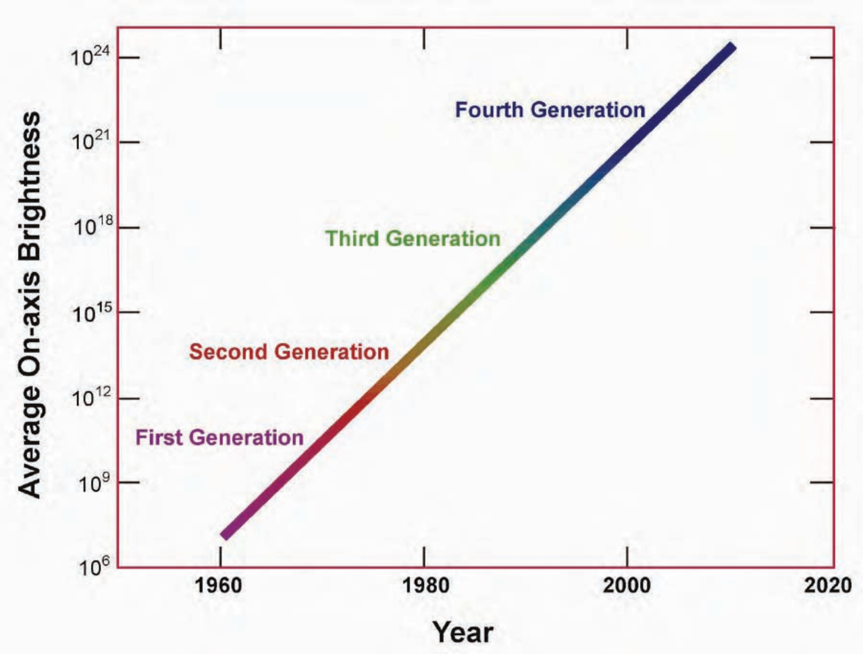
Neutrons can be generated through nuclear reactions, released as products of the decay of radioisotopes, or knocked free from an atomic nucleus by another particle accelerated to high energy—a process known as spallation. Neutron sources can be further categorized as continuous or pulsed. High flux reactors are used to generate neutrons at two of the five major neutron scattering centers operating in North America. Two major North American neutron scattering centers in operation at the time of the workshop (the Neutron Science Center at Los Alamos National Laboratory and the Intense Pulsed Neutron Sourceat Argonne National Laboratory) utilize a pulsed linear accelerator to produce spallation neutrons with polychromatic wavelengths. The reactor-based sources produce thermal or cold neutrons well-suited to structural investigations, but share a major disadvantage with most neutron facilities in the world—low flux with continuous or defined energies. To compensate, researchers must use large samples and increase the duration of their experiments, steps that can sometimes limit the scope of their investigations. New accelerator-based sources and creative instrumentation developed over the last decade have improved this situation tremendously, but neutron flux is still often at a premium.

At least 29 countries now host more than 60 major x-ray scattering centers, deriving their beams from synchrotrons. While Japan has the greatest number with 12 centers, there are presently 7 such facilities in the United States, with powerful new sources under construction or beginning operation around the globe. U.S. x-ray facilities include:

- Advanced Light Source, Lawrence Berkeley National Laboratory (ALS)
- Advance Photon Source, Argonne National Laboratory (APS)
- Center for Advanced Microstructures & Devices, Louisiana State University (CAMD)
- Cornell High Energy Synchrotron Source, Cornell University (CHESS)
- National Synchrotron Light Source, Brookhaven National Laboratory (NSLS)
- Synchrotron Radiation Center, University of Wisconsin-Madison (SRC)
- Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center (SSRL)

Generations of Synchrotron Radiation Sources

The production of x-rays by relativistic electrons in accelerators is about 60 years old. The accelerator facilities used as synchrotron radiation sources have advanced significantly over the years, growing in utility to become a premier research tool for the study of materials. The evolution of these facilities is typically described as a sequence of generations of synchrotron radiation sources, as shown in Figure 1.1 below. The *first generation sources* were electron synchrotrons and electron storage rings originally designed and operated for high-energy or nuclear physics. These facilities were adapted for use as synchrotron radiation sources by adding exit ports for the radiation. They were initially run in a parasitic mode, with some accelerators later repurposed for use solely as synchrotron radiation sources. The *second generation sources* were electron storage rings dedicated to production of synchrotron radiation. They were designed and optimized specifically for light production. In the 1990's, the *third generation sources* started operation. These facilities provided orders of magnitude greater brilliance by a combination of reduced emittance of the electron beam and use of undulators as the primary source of radiation. *Fourth generation sources* are currently being designed and demonstrated. Two approaches have been proposed, both employing a linear accelerator, or linac, instead of or in addition to a circulating storage ring for the production of ultralow emittance and ultrashort electron bunches as the source of radiation. With a very long undulator placed at the end of a suitable linac, sub-picosecond pulses of coherent radiation can be produced with peak brillance many orders of magnitude greater than third generation sources. These *free electron lasers* operate by either self-amplified spontaneous emission or by seeding with external pulsed laser synchronized to the electron bunches. Or, a recirculating linac can be incorporated into a storage ring facility to decrease the emittance at a strategic location while allowing other insertion devices to run in parallel. When the recirculated electron bunches return energy back into the linac, the *energy recovery linac* allows for more energy efficient operation comparable to third generation sources. The chart below illustrates the continued improvement of brightness for each successive generation of synchrotron x-ray sources.



Development of Synchrotron Radiation Sources

More than a dozen large-scale neutron facilities in the Americas, Europe, and across Asia and Russia provide research and development opportunities for scientists from around the globe (see www.neutronscattering.org/Links/links.htm).

U.S. neutron facilities include:

- High Flux Isotope Reactor Center for Neutron Scattering, Oak Ridge National Laboratory (HFIR)
- Intense Pulsed Neutron Source, Argonne National Laboratory (IPNS)
- Los Alamos Neutron Science Center, Los Alamos National Laboratory (LANSCE)
- NIST Center for Neutron Research, National Institute of Standards and Technology– Gaithersburg (NCNR)
- Spallation Neutron Source, Oak Ridge National Laboratory (SNS)

The U.S. Department of Energy (DOE), Office of Basic Energy Sciences operates eight major light and neutron user facilities, which collectively support over 10,000 users per year for research across all physical science disciplines. The National Synchrotron Light Source at the U.S. Department of Energy's (DOE) Brookhaven National Laboratory, for example, presently provides essential scientific tools to over 2,500 scientists per year from more than 400 academic, industrial, and government institutions. The National Science Foundation (NSF) supports two major x-ray facilities, each serving over 500 scientists, graduate students and researchers each year—CHESS and SRC). The National Institute of Standards and Technology (NIST) in partnership with the NSF supports over 1,000 users a year at NCNR.

Each of the major scientific x-ray and nuclear facilities feature multiple beam lines and extensive associated instrumentation. The number of facilities continues to grow, and they are used by more scientists every year, both in the United States and worldwide. The sophistication of these facilities is also increasing. New developments in instrumentation for elastic, inelastic, and magnetic scattering are extending their capabilities. Improved sample cells and preparation facilities now make it easier for researchers to perform experiments on samples maintained at ultrahigh to ultralow temperatures, under extreme pressure or in vacuums, and in controlled chemical and magnetic environments.

Europe invests $200 million in operating its neutron reactors each year. Japan has invested over $3 billion in construction of pulsed neutron sources in the last 10 years. While U.S. capacity has been increased through recent Federal support for upgrading existing x-ray and neutron sources, developing new sources, and improving instrumentation, the demand for state-of-the-art focusing devices, tools, and cyber infrastructure can not presently be met. To remain at the cutting edge of many areas of science, engineering, and technology—including nanotechnology—the United States must maximize its investment in maintaining and upgrading present U.S. x-ray and neutron sources and instrumentation.

Construction costs for a state-of-the art x-ray or neutron facility can easily exceed $1 billion. Annual operating expenses—including the cost of electricity, facilities management, and staffing for user centers—may range from several million dollars for a smaller facility to $150 million or more for the largest facilities.

New major light and neutron user facilities are under construction or planned in the United States. Since the completion of the workshop, a major milestone in U.S. pulsed neutron source generation has been reached at the DOE's Oak Ridge National Laboratory. The Spallation Neutron Source began operating in 2006, and is now the world's most intense pulsed neutron source. When fully instrumented, it will provide the international community with open user access to 24 beamlines on a merit-review basis. At full capacity it will host thousands of academic, industrial, and government researchers each year. A new state-of-the-art medium energy storage ring is under construction at Brookhaven National Laboratory as an upgrade to the National Synchroton Light Source. When completed, NSLS-II will deliver deliver x-rays up to 10,000 times brighter than those produced at the NSLS today and will feature continual restoration of the current in the storage ring to provide constant light output. The upgrade will extend the power of x-ray scattering techniques as applied on nanometer length scales by facilitating the development of novel full-field x-ray imaging procedures and by focusing x-rays down to 10 nm or below.

In 2009, the DOE's Linac Coherent Light Source (LCLS) at the Stanford Linear Accelerator is expected to become operational, delivering x-rays with peak brightness a billion times that of existing sources. The LCLS will be the world's first free electron laser (FEL) producing x-rays at nanometer or shorter wavelengths. A new class of storage-ring-based synchrotron sources known as energy recovery linear accelerators (such as that under development at Cornell University with the support of NSF) could provide similar increases in brightness, as could the free electron lasers planned by an MIT-University of Wisconsin team for operation in the VUV and soft x-ray regions of the spectrum. These brilliant next-generation sources with their unprecedented combination of brightness, flux, spatial and temporal coherence, and advanced optics will transform synchrotron science, enabling new experiments to probe phenomena or modify material properties at the nanoscale. One can imagine performing *in situ* experiments on an individual nanometer-sized catalyst particle in actual reaction conditions; performing x-ray experiments on a single carbon nanotube while electric current is passing through the nanotube; using coherent lithographic techniques to fabricate novel structures; and developing a variety of new techniques to explore complexity at the nanoscale, monitor the dynamics of biomolecules, measure two-time correlations in chemical reactions, and create nanoscale modifications in the structure of materials.

1.2 OVERVIEW OF X-RAY AND NEUTRON SCATTERING FOR NANOSCALE SCIENCE AND NANOTECHNOLOGY RESEARCH

Researchers visiting U.S. light sources and neutron scattering facilities tackle fundamental and applied problems in science and technology ranging from biology, chemistry, and physics through materials and environmental science, geology, and engineering, to medicine and health science. Nanoscale phenomena are central to all these disciplines, and these disciplines often intersect at precisely this scale. The special opportunities that x-rays and neutrons offer for characterization, analysis, and interpretation at these unique facilities are therefore poised to make important contributions to nanoscience and nanotechnology. Experiments to analyze and characterize superconductors, low-dimensional solids, cells, tissues, minerals, magnetic materials, and myriad other samples at x-ray and neutron facilities have already allowed scientists to discover new physical properties and solve problems across engineering, science, technology, and medicine. Researchers use scattering facilities to address critical problems of national importance such as environmental remediation and energy related issues, potentially saving U.S. citizens millions in tax dollars, and also contribute to economic development through discovery and innovation.

As tools of the nanoscience and nanotechnology revolution, these powerful scattering sources provide scientists with intense x-rays and neutrons to characterize and assist in fabricating nanostructured materials, nanoscale devices, and nanosystems. As subatomic probes of dynamics, these scattering centers and specialized instruments allow research scientists to literally make movies of nanostructures and nanomaterials—either human-engineered or biological—in motion at the nanoscale. Nanoscience researchers at brilliant next-generation synchrotron light sources and spallation neutron accelerators are already:

- watching self-assembly and directed self-assembly of nanomaterials
- making tribological measurements on nanosystems
- creating nanomagnetic materials with novel properties
- manufacturing superhard materials under pressure

Worldwide, large-scale light and neutron facilities are advancing research and development in diverse fields including:

- biosciences
- medicine
- chemical and environmental sciences, agriculture, minerals exploration, materials engineering, microsystems and nanosystems engineering
- forensics
- geophysics

Scientists are using x-rays and neutrons as nanoprobes for:

- solving the crystal structures of proteins
- imaging tumors with high resolution during advanced radiation therapy
- understanding catalytic processes in toxicology measurements, atmospheric research, and green manufacturing
- investigating plant genomics
- imaging nanostructured materials, ceramics, and intelligent polymers
- tracking the mechanical response of nanostructured light metals and alloys under applied heat and pressure
- studying fatigue in metal oxide electronic and magnetic materials
- imaging cracks and atomic defects in structures with high resolution in real time

While the brilliant and intense sources, advanced characterization techniques, and novel instrumentation found at our x-ray and neutron scattering centers have been essential to these investigations, they are not by themselves sufficient. They must be combined with cutting-edge theoretical descriptions, models, and simulations. Physically based multiscale models now play a central role in understanding the behavior and properties of engineered nanomaterials and in developing rational design methods for nanostructures. The development and validation of advanced software for multiscale modeling requires collaboration among theorists and experimentalists across disciplines.

Profound questions about atomic structure and molecular dynamics, which are central issues in nanoscience, may well be answered through this combination of approaches. Significant progress is already being made. Researchers at the Advanced Photon Source at Argonne National Laboratory–the country's most brilliant source of x-rays for research—have been able to create a detailed picture of how atoms rearrange themselves inside nanostructured devices. At the Synchrotron Radiation Center at University of Wisconsin–Madison, x-rays are being used to take a miniature look into the surface chemistry and nanotribology underlying friction and lubrication mechanisms in nanoelectromechanical systems. Investigations of the electronic structure of complex oxide systems, performed with intense x-rays from the National Synchrotron Light Source at Brookhaven National Laboratory, are helping researchers design new classes of catalysts.

Effective utilization of our x-ray and neutron resources, and further smart development of those tools, will continue to bring new insight into nanoscale phenomena and properties that will impact diverse application areas such as catalysis, photovoltaics, fuel cells, membranes, adsorbants, coatings, displays, ceramics, thermoelectrics, adhesives, sensors, batteries, pharmaceuticals, and magnetic and semiconducting devices.

1.3 OVERVIEW OF THE WORKSHOP

To clearly identify and articulate the relationship between nanoscience and nanotechnology R&D and the nation's x-rays and neutron resources, a workshop was convened on June 14-16, 2005 in Washington, DC under the auspices of the National Nanotechnology Initiative. The meeting was jointly sponsored by the U.S. Department of Energy, the National Science Foundation, and the National Institute of Standards and Technology, and endorsed by the Nanoscale Science, Engineering, and Technology Subcommittee of the Committee on Technology, National Science and Technology Council. Chapter 2 of this report recounts the discussions and deliberations of that workshop, and Appendix C compiles the abstracts of individual contributions.

The workshop brought together over 150 scientists, engineers, and policy makers to discuss the relationship between x-ray and neutron science and the research and development activities of the NNI. The chairs of the workshop drew upon the deliberations, discussions, and summary findings of all the participants to plan a roadmap for the development of x-ray and neutron scattering sources and instrumentation over the next 20 years. They also identified the most promising and urgent applications of these advanced resources to nanoscale research and technology. These applications are presented in Chapter 3 as research target areas. The roadmap—presented in Chapter 4—and this workshop report will guide universities, researchers, industry, governmental agencies, and policy makers interested in the use of x-ray and neutron scattering to ensure progress in R&D at the nanoscale.

A central reason for holding the workshop and preparing this report is to make the broader scientific community aware of opportunities to use the open-access—often free—x-ray and neutron user facilities available at U.S. universities and national laboratories. The U.S. Government has made a significant investment in these facilities over the past five decades to ensure the competitiveness of the United States in science and technology, and it is important that they be fully utilized to advance nanoscale science, engineering, and technology.

The workshop began with morning plenary sessions which explored frontier problems in nanoscience. Twenty-five invited presenters showed how x-ray or neutron scattering techniques can elucidate issues that cut across various scientific disciplines, such as understanding interfacial structures; characterizing nanosystems; studying confinement; and probing self-assembly process in hard materials, soft materials, or biomaterials. Afternoon breakout sessions featured contributed presentations and group discussions organized around six topics:

- x-rays and neutrons for synthesis of nanomaterials
- x-rays and neutrons for self-assembly and directed self-assembly

- x-rays and neutrons as probes of novel properties: emerging functionality at the nanoscale
- multiscale theory, modeling, and experiment
- advanced x-ray and neutron techniques
- advanced characterization for nanomaterials

The last two topics have been combined in the remainder of this report.

Two key questions underlied the discussions in the breakout sessions:

1. Which outstanding problems in nanoscale synthesis, structure, dynamics, and properties can be addressed using x-ray and neutron techniques such as scattering, imaging, and spectroscopy, and how can these techniques help illuminate the important and urgent issues at the nanoscale?
2. How might the current resource base in x-ray and neutron scattering techniques be augmented to make it even more capable of solving outstanding problems in nanoscale science?

Brief summaries of the material discussed in each breakout section are found below, and abstracts of individual presentations contributed to these sessions are found in Appendix C. A special workshop session was held featuring poster presentations by scientists in the early stages of their research careers. The graduate students, postdoctoral research associates, and junior faculty participating in this session were selected to attend the workshop through a competition. Applicants submitted a description of their interests in applying x-ray and neutron techniques at the nanoscale, and gave their own thoughts on the two key questions above. A list of the selected participants appears in Appendix B.

X-rays and Neutrons for Synthesis of Nanomaterials

The central target in nanomaterials research is learning to produce nanoscale materials with optimal properties for a specific application by gaining control over composition, structure, defect density, interface properties, and function. These material properties involve features at the full hierarchy of lengths from sub-nanometer to centimeter—atomic scale, nanoscale, microscale, and macroscale. To gain control of the range of material properties, the community seeks a fundamental understanding of nanoscale chemistry and physics and of the laws that govern physical scaling. New tools for characterizing the structure, composition, properties, and dynamics of materials at the nanoscale will provide the scientific foundation for that understanding and accelerate the pace of discovery. There is a pressing need for real-time, *in situ* monitoring of the synthesis and processing of nanomaterials to study kinetics, mechanisms of nucleation and growth, structure-property-processing relationships, and the control of defects and interfaces. X-ray scattering, x-ray fluorescence, x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS) are well suited to probing synthetic processes at the atomic scale that are difficult or impossible to study with traditional electron imaging or spectroscopy techniques.

X-rays and Neutrons for Self-Assembly and Directed Self-Assembly

Self-assembly driven by thermodynamics and directed self-assembly guided by external fields are important mechanisms for forming heterogeneous nanoscale structures. X-rays and neutrons will have an important role in determining the nanoscale structure of self-assembled systems and measuring the interactions among particles. This is a necessary first step towards achieving full control of the self-assembly process, which would have far-reaching scientific and technological implications. Biology provides ample examples of self-assembly at work; for example, in the formation of many subcellular structures including the cytoskeleton. The multitude of structural morphologies exhibited in nature has lent much inspiration to those who design and produce engineered nanostructured materials. The benefits of self-assembled nanostructured materials are being explored for a broad range of applications, including drug and gene delivery agents, nanoporous membranes, and miniaturized biosensor arrays. One recent success is the use of neutron reflectivity experiments to obtain density distribution profiles of adsorbed diblock polymers with detail at the molecular level. When combined with state-of-the-art techniques for polymerization and selective deuteration, and then applied to controlled model architectures, neutron reflectivity measurements will help elucidate the structure of complex systems at interfaces under confinement and applied shear stress. Many other advanced neutron and x-ray scattering techniques can contribute in this area; for example, grazing incidence diffraction could yield even more in-plane detailed structural information.

X-rays and Neutrons as Probes of Novel Properties: Emerging Functionality at the Nanoscale

An understanding of novel properties at the nanoscale and their relation to function will stimulate new research and development activities across diverse application areas such as catalysis, photovoltaics, fuel cells, membranes, adsorbents, coatings, displays, ceramics, thermoelectrics, adhesives, sensors, batteries, pharmaceuticals, and magnetic and semiconducting devices. At the nanoscale frontier of semiconductor science and technology, there is intense experimental and theoretical research into devices ranging from high-electron-mobility transistors, to semiconductor lasers and other optoelectronics, and to quantum Hall effect devices. At the analogous frontier in the magnetics industry, researchers are developing and exploiting new quantum-engineered materials, artificially structured at the atomic level, to produce the magnetic properties desired for ultradense data storage or spintronic devices.

X-ray and neutron facilities can probe the structural, chemical, and electronic properties of materials at the atomic level with excellent temporal resolution. Innovative instrumentation allows simultaneous measurements of multiple properties yielding experimental data that better describes real-world conditions. Inelastic neutron scattering (INS) is being used effectively to study the adsorption, entrainment, and reactivity of molecules and reaction intermediate species, especially those containing hydrogen. New spectroscopic neutron instrumentation will soon be able to provide chemical information analogous to infrared Raman spectroscopy while simultaneously determining structure. Newly available environmental cells are critical to these investigations, allowing elastic and inelastic scattering studies to be performed *in situ*.

Advanced Techniques for X-rays and Neutrons

While today’s x-ray and neutron techniques are well suited to following the structure and dynamics of materials on the nanoscale, there is substantial room for improvement. Better devices for manipulating and focusing beams, improved detectors, instrumentation built around dedicated sample environments, and more sophisticated or more flexible environmental controls can sharpen the spatial and temporal capabilities of these techniques; extend the domain to which they are applicable; and make them more easily accessible to a wider variety of researchers. As the size of x-ray beams shrinks into the 1–10 nm range, scattering, x-ray fluorescence, x-ray absorption fine structure, holography, tomography, and incoherent and coherent diffraction have the potential to revolutionize nanocharacterization. Future detectors for x-ray reflectivity and surface crystallography measurements will feature faster readout, larger dynamic range, and improved energy resolution. Neutron lenses and focusing techniques are also improving rapidly. Newly emerging focusing methods, together with improvements in reflective nondispersive mirrors and refractive dispersive magnetic lenses, will allow researchers to tailor neutron beams to spot sizes smaller than 100 nm. Advanced focusing methods for both x-rays and neutrons will extend measurements to much smaller sample volumes while maintaining maximum flux at the sample.

Multiscale Theory, Modeling, and Experiment

To more fully exploit scale hierarchies in nanostructured materials, both computational and experimental probes must be specifically designed to investigate multiple time and length scales. Techniques for the rational design of nanostructures with desired novel behavior, response, and properties will depend on these multiscale tools. Physics- and chemistry-based models must be validated through collaborative research efforts involving theory, experiment, and simulation that range over multiple scales and cross disciplinary boundaries. An example of the current state of the art is structure determination for imperfect nanocrystals. Significant progress has been made by applying the atomic pair distribution function (PDF) method to analyze total diffraction data from neutron or x-ray experiments.

Key Workshop Findings

Several areas in nanoscience that x-ray and neutron techniques can uniquely address emerged from workshop discussions, including:

For x-rays:

- structural, chemical, magnetic, and dynamic properties of individual and ensembles of nanoparticles
- determination of crystallinity, or texture, in, for example, nanocomposites
- fluorescence and absorption to determine elemental composition, and bonding states at the nanoparticle-environment interfaces under real conditions
- reflectometry of interface/surface structure in films, multilayers, and nanoparticles
- structure characterization of macromolecules, proteins, and nanoparticles
- *in situ* characterization of self-assembly processes and growth processes
- direct probing of catalytic activity in realistic environments, including both surface and internal chemistry and structure
- coherent diffraction/scattering to determine structure in non-periodic nanoparticles, including defects and strain
- dynamics using a complement of real-time and energy-loss techniques from attoseconds to seconds to investigate processes such as protein folding, entangled polymers, and glassy dynamics
- ultrafast dynamics of chemical reactions, charge transfer, and other processes that occur on time scales below femtoseconds in nanodevices

For neutrons:

- structure (nuclear and magnetic) of thin films using neutron reflectometry
- structure of macromolecules (polymers, proteins, and nucleic acids) over length scales on the order of 1 to 100 nm using small-angle neutron scattering
- structure of nanoparticles, using total scattering methods and analysis of pair distribution functions

- structure and dynamics of adsorbed species, reaction intermediates, and chemical products on metal-oxide supports and heterogeneous catalyst surfaces under reaction conditions
- *in situ* dynamics of protons in hydrogen-bonded materials
- *in situ* dynamics in confined systems
- spin dynamics (both individual and correlated) of molecular magnets and assemblies of magnetic nanoparticles
- bonding of nanocoatings to surfaces

The editors of this report, with the help of the workshop organizing committee, have analyzed the community's input and organized their recommendations into seven cross-cutting research target areas. These areas encompass the most promising nanoscale applications of x-ray and neutron scattering and imaging analysis, and identify critical needs for advanced instruments and novel techniques.

The seven research target areas thus selected are:

- **Dynamics: Lessons for Nanotechnology from Nature.** The scientific community often seeks inspiration from nature as it strives to build new functional nanomaterials. In biological materials, dynamic processes have been developed and refined over millions of years. They cover an enormous range of time scales, from the fast electron transfers of bonding processes or photosynthesis, through molecular vibrations, to folding of proteins and wrapping of nucleosomes. As new techniques, upgraded sources, and improved instrumentation move the temporal resolution of x-ray and neutron scattering from milliseconds to attoseconds, they will provide insight into dynamic processes across a range of disciplines.
- **Nanomaterials: Understanding the Impact of the Real World.** A major challenge in nanomaterials R&D is to understand and control stability of nanomaterials in real, variable environments and their response to those changing environments (e.g., varying temperature, pressure, electric or magnetic fields, stress or shear, gaseous exposure, or pH). Neutron scattering studies of particle size distribution and degree of local disorder are valuable probes of real-world materials including nanocatalysts (which are becoming ubiquitous in applications ranging from automobile catalytic converters to high-volume industrial processes) and mechanically loaded polymers. X-ray scattering provides nanometer-length-scale measurements in soft matter systems and nanoscale structural information regarding singular defects in self-assembling or catalytic materials.
- **Extreme Environments.** Subjecting nanomaterials to extreme conditions—pressure in the 100s of gigapascals, temperature of 1000 °K or a few millidegrees, large static and dynamic deformations, electric fields of many kV/cm, or magnetic fields in the 10s of teslas—can drastically alter material behavior, produce unique physical properties, and create superior materials performance. For example, at high pressures, gases can become superconductors; novel electronic, magnetic and superhard materials can be formed; unreactive noble elements can be made reactive; and new chemical and biochemical pathways can be switched on. Continued development of environmental cells, which take advantage of the ability of x-rays and neutrons to probe materials in extreme environments, will allow scientists to precisely tune physical, chemical, and biological properties of nanomaterials and mimic conditions found in exotic locations such as extrasolar planets or deep within the earth's mantle.
- **User-Friendly Modeling: The Nano Toolbox.** Understanding the relationship between structure, properties, and function in naturally occurring and engineered nanostructures poses exceptional

challenges, given their diversity and richness. If researchers from a variety of disciplines have at their disposal an integrated modeling toolbox filled with analysis programs, graphical tools, scripts, and interfaces to x-ray and neutron datasets, they can harness and integrate structural, dynamic, and response data to provide deep insights into nanoscale structure/properties and to enable nanomaterials by design. We envision a collection of tools that can be individually tailored to, and are developed by, individual researchers. Each researcher's Nano Toolbox would reside on several nodes of the universal computing grid, as well as on local resources.

- **Nanoparticles: The Ultimate in Precision Metrics.** Future applications of nanotechnology will rely on new nanoscale materials or devices whose functionalities emerge from the controlled introduction of individual atoms, electrons, or spins into a host nanoparticle or matrix. To develop these applications, researchers require the ability to identify the position of an individual atom within a nanoparticle with picometer precision, determine its chemical bonding state, and fully map the structure of the surrounding atoms in three dimensions. Improved sources, focusing optics, and detectors can extend advanced x-ray spectroscopy and scattering methods to single-atom sensitivity.
- **Next-Generation Electronics: Following a Single Spin.** The operation of spintronic devices, often envisioned as next-generation successors to electronics, depends on structures for injecting and manipulating individual electron spins. The ability to follow a single spin moving through a prototype device would greatly accelerate the design and testing of these spin-based devices. Soft x-ray resonant magneto-optical techniques using third-generation synchrotron sources can already measure the activity of a small number of electronic spins; extension to individual spins should be pursued. Polarized neutron reflectometry can profile both the magnetic and structural properties of layered heterostructures with .01 nm resolution and can determine vector orientation of the local magnetic moments. Recently developed neutron spin manipulation techniques will enable spin orientation to be determined at surfaces with lateral dimensions ranging from nanometers to microns. Future neutron scattering techniques will provide attosecond snapshots of magnetic materials.
- **Nanoprocessing and Nanomanufacturing.** X-rays and neutrons have great potential as tools for direct fabrication of novel nanostructures and as *in situ* diagnostic tools for other nanomanufacturing processes. We envision that x-ray nanobeams will be used to write two- and three-dimensional structures by nonlinear photochemical interactions. X-rays can write at buried interfaces and fabricate high-aspect-ratio structures deep within the sample matrix. The range of processes that can be stimulated in a material by neutron or x-ray waves includes phonons, spin waves, electronic transitions, atomic transitions, and local heating. Ultracoherent waves from next-generation x-ray sources (based on free electron lasers) can be used to create standing waves, holograms, and traveling waves in layers.

The meeting chairs then constructed a roadmap for accelerating R&D across these target areas over the next 5, 10, and 20 years. This roadmap suggests priority investments in ultrafast dynamics, bridging from nano to micro, single-particle characterization, real environments, and cyberinfrastructure. It describes advanced, futuristic techniques as far ranging as 1 nm optical imaging, with hard x-ray probes, x-ray-based nanomanufacturing and assembly processes, time modulation neutron holography, neutron spin echo techniques to label individual atoms in nanostructured materials, and attosecond time stamping enabled by free-electron laser sources.

2. WORKSHOP SESSION SUMMARIES

This chapter summarizes the presentations, deliberations, and discussion of the workshop breakout sessions and the special early-career poster session. The six breakout sessions at the workshop were chosen to cover the breadth of science and advanced techniques required for fruitful discussion. These six breakout sessions were: Synthesis; Directed and Self-Assembly; Novel Properties; Advanced Technique Development; Advanced Characterization for Nanomaterials; Theory and Modeling. In this section, Advanced Technique Development and Advanced Characterization for Nanomaterials are combined into one summary section.

2.1 X-RAYS AND NEUTRONS FOR SYNTHESIS OF NANOMATERIALS

Led by Phillip Britt, Oak Ridge National Laboratory, and Robert Hull, University of Virginia

To date, most nanoscale materials and their properties have been discovered by an empirical or Edisonian approach. To realize the broad benefits of nanomaterials, the kinetics, mechanisms, and thermodynamics of nanoscale synthetic processes must be understood, as well as the fundamental relationship between structure, property (including reactivity), and function. The ultimate goal is *science-driven synthesis* (also called *materials by design*), in which nanomaterials are produced for a specific application with a predetermined composition, structure, defect density, interface property. These nanomaterials incorporate function on length scales from atomic to nano to micro to macro through a fundamental understanding of nanoscale chemistry and physics and the laws that governing physical scaling. To achieve this goal, new approaches need to be established for synthesizing nanomaterials and nanomaterial building blocks, and the rules governing self-assembly or directed self-assembly needs to be defined for the construction of hierarchical structures. To accelerate the pace of discovery and to provide the scientific foundation for discovery, new nanoscale characterization tools are needed to characterize the structure, composition, properties, and dynamics of nanometer-sized objects.

Scanning electron microscopy (SEM) can provide a two-dimensional (2-D) top view of nanoscale structures after synthesis. Scanning probe technologies such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM) are widely used to image the surfaces of nanostructures, and can often add topographic information (sometimes called 2½-D). Transmission and scanning transmission electron microscopies (TEM and STEM) provide information from within samples, but the specimens used must be very thin (typically from a few nm to a few μm) because of the strong interactions of accelerated electrons with matter. The ability of x-ray and neutrons to penetrate the sample allows them to probe the full three-dimensional (3-D) structure and composition of nanoscale materials and interfaces while minimizing or eliminating sample damage. The unique contrast mechanisms available and the extensive range of accessible length and time scales are additional advantages of x-ray and neutron techniques for *in situ* investigations of structure and dynamics. Neutrons, as a consequence of their magnetic moment, and polarized x-rays are well suited to study (the depth dependence of) magnetic domains and magnetic transitions in magnetic materials (i.e., nanomagnetism). Neutron scattering is the preferred method to study the structure and dynamics of soft materials (i.e., polymer and biomaterials) because of several advantages: hydrogen/deuterium substitution provides an excellent contrast mechanism; macromolecular conformation can be studied in the bulk, in solution, or at interfaces; and the meV energies of neutrons (compared with keV energies for x-rays) minimize damage to radiation-sensitive samples.

Over the past three decades, small-angle x–ray scattering (SAXS) and small-angle neutron scattering (SANS) have been widely used to study structure and dynamics in polymer science, materials science, and structural biology. Small-angle scattering techniques are still well-suited to studying some structural, compositional, and dynamic aspects of nanomaterials under a variety of process conditions (temperature, pressure, and shear). However, many current questions being asked in nanoscience and nanotechnology are tougher. Meeting these research challenges will require a higher spatial, temporal, and energy resolution than is now available, and will push neutron and x-ray techniques and their associated data analysis techniques to their limits.

There is a pressing need for real-time, *in situ* monitoring of the synthesis and processing of nanomaterials to study fundamentals of the kinetics and mechanisms of nucleation and growth of nanomaterials, structure-property-processing relationships, and the control of defects and interfaces. Many synthetic processes are difficult to probe at the atomic scale by traditional electron imaging or spectroscopy techniques, but x-ray scattering and spectroscopy are ideally suited for real-time, *in situ* investigations of atomic-scale mechanisms, binding, composition, and structure. Techniques such as x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS, which includes x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS)) can be applied to study vapor phase processing methods (chemical vapor deposition (CVD), metal organic CVD (MOCVD) (see Fig. 2.1 and Ref. 1)), and atomic layer deposition (ALD), as well as etching methods such as reactive ion etching (RIE), and solution phase growth methods such as the sol-gel process. These studies will help unravel the complex relationship between the experimental parameters and resulting structure. They will provide insights into the creation of non-equilibrium or metastable structures and into new synthetic methodologies, and they will improve our understanding of the fundamental relationships among structure, property, and function. This understanding will lay the foundation for significantly expanded nanomaterials development.

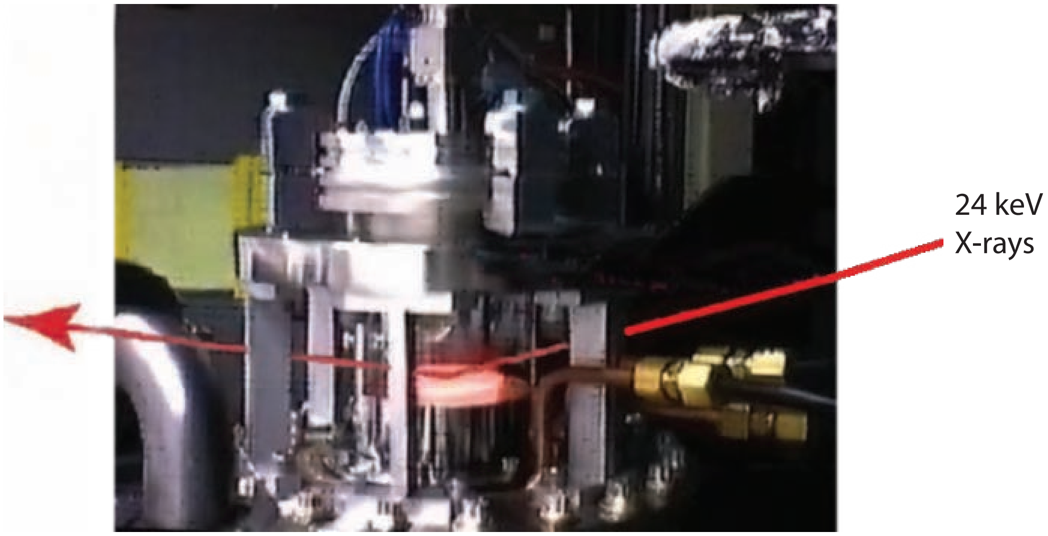


Figure 2.1. Hard x-rays can be used to investigate the real-time formation of PbTiO3 films grown in this vertical flow metal organic chemical vapor deposition chamber, monitoring the behavior of the ferroelectric phase as a function of film thickness. (Courtesy G.B. Stephenson, Argonne National Laboratory.)

One area that would greatly benefit from *in situ* synthetic investigations is epitaxial growth of two-dimensional (thin layers), one-dimensional (wires), and zero-dimensional (quantum dot) structures. Such structures enable confinement of electronic carriers, engineering of quantum properties, and ultimately control of electronic (charge) and magnetic (spin) properties at the single-electron level. The synthesis and characterization challenges include the need to understand the time evolution of structures and properties, to measure chemical composition in extremely small structures (< 1 nm), to determine the presence of electrically active impurities (dopants), to measure surface and subatomic structure with atomic precision, and to map strain fields. *In situ* x-ray (and potentially neutron) diffraction and spectroscopy tools would revolutionize the understanding and control of heteroepitaxial structures and provide insight into structure-property relationships for zero-, one-, and two-dimensional structures.

Grazing incidence small-angle x-ray scattering can be used to follow the kinetics of monolayer formation and nanoparticle growth, film density, thickness, and roughness, and the self-organization of (bio) macromolecules at interfaces. These techniques are also good for depth profiling, which is needed to study multilayered structures, such as those found in complex metal oxides, and for the study of buried interfaces, such as those found in a variety of materials ranging from grain boundaries in nanograined materials to nanocomposites.

To take full advantage of the benefits provided by x-rays and neutrons for *in situ* studies, a variety of specialized sample environments need to be constructed. These should be optimized for the particular beam line and detector geometry and should provide appropriate reaction environments for synthesis, such as a chemical vapor deposition chamber. To optimize the use of beam time, these specialized synthesis environments should also be designed so that experiments can be run off-line. Additional sample environments are also needed, providing control over processing variables such as temperature, pressure, shear, and magnetic or electric field for solid, liquid, or colloidal samples. Sophisticated data analysis and modeling software should provide real-time results so that the impact of the reaction parameters (temperature, concentration, external field, etc.) can be followed in real time. Sample environments allowing researchers to take advantage of multiple characterization tools are especially desirable. Measurement of SAXS data simultaneously with imaging via optical microscopy would help bridge the gap between our nanoscale and microscale descriptions of materials. Simultaneous measurement of structural properties and physical properties such as hardness, conductivity, catalytic activity, and magnetic, optical, electronic, thermoelectric, or piezoelectric response would also help define relationships between structure and properties.

With current wet chemical, gas-phase, and laser-based synthetic techniques, it is sometimes difficult to accurately control the levels of defects, atomic composition, domain size, and order distribution, of many nanomaterials. When the relationship between nanoscale structural precision (i.e., defect density) and the resulting macroscopic properties is not known, characterization tools are needed to determine the consequence of a single lattice defect (vacancy), a single impurity atom, a surface step, a dislocation, or strain on the bulk structure, properties, and chemical reactivity. In magnetic materials, a defect, compositional change, or strain can alter the magnetic exchange length and create a dramatic change in macroscopic magnetic properties. In semiconductors, structural and compositional defects quench the flow of electrons, holes, and excitons, reducing the efficiency of photovoltaic devices. However, in catalytic materials, structural defects may be desirable since they could be the "active sites" responsible for the enhanced chemical reactivity. Thus, to optimize the properties of these nanomaterials, atomic-level, element-specific synthetic methods are needed, as well as structural and elemental probes with resolution of < 1 nm. *In situ* nanoscale probes could revolutionize our understanding of the correlation between nanoscale structure and macroscale properties and change our approach to the synthesis of nanoscale materials to provide reproducible control over defects, a key challenge in scaling up production of nanomaterials and nanodevices for commercial applications.

Visualization of the arrangement of atoms and structural morphologies has played a crucial role in the advancement of nanoscience and nanotechnology. Visual clues can also be very helpful in modeling complex scattering data. Widespread availability of 3-D imaging and visualization tools is a critical need as nanomaterials are assembled into increasingly complex hierarchical structures—progressing, for example, from nanoparticles to dispersions to composites to aligned nanostuctures. Three-dimensional images aid in correlating the structure of a material with its properties, and provide insight into changes in internal structure. The latter is especially important for biomolecules in studying, for example, the collapse of pores, migration of an internal interface, or rearrangement of a membrane protein during processing, in response to binding of a specific solute, or under a stimulus. Understanding such changes could suggest new methods for stabilizing structures and give insight into the mechanisms of reactions (especially for macromolecules).

A novel approach is to design the sample specifically to take advantage of the characterization method. For example, highly correlated electronic systems and structurally similar complex oxides are currently of significant interest since they exhibit unexpected phenomena, such as high-temperature superconductivity, colossal magnetoresistance, and ferroelectricity. The unusual properties of these materials arise from self-organization at the nanoscale, and x-ray and neutron scattering have been fundamental in revealing the materials' associated nontrivial electronic structure. Unfortunately, the most revealing neutron scattering studies require single-crystal samples of significant size. Conventional bulk crystal growth methods offer limited capacity to design and tune the crystal structure or to make completely artificial crystals. Thus, a new synthetic method, pulsed laser deposition, was developed to grow micrometer-thick metal-oxide heterostructures with atomic-layer control of dissimilar metal oxides and complete reproducibility of the interface over thousands of unit cells (see Fig. 2.2).

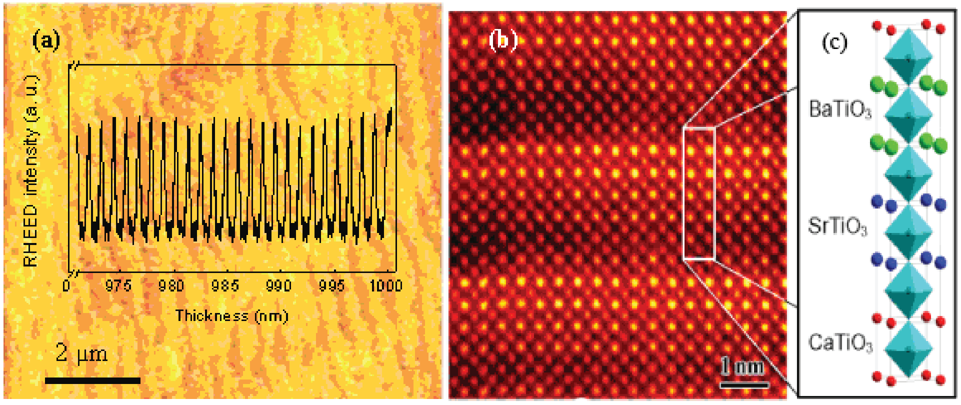


Figure 2.2. An artificial ferroelectric-dielectric superlattice with compositionally abrupt interfaces between layers of barium titanate, strontium titanate, and calcium titanate was synthesized with atomic-scale control by high-pressure pulsed laser deposition. (a) Reflection high-energy electron diffraction data overlayed on an optical micrograph of the superlattice which contains thousands of unit cells with completely reproducible surface and interfacial quality. The regular oscillations in the diffraction data indicate uniform growth of the unit cells out to 1 mm. (b) Cross-sectional Z-contrast scanning transmission electron micrograph of the compositionally abrupt interface. (c) Diagram showing the atomic structure of the superlattice. The light blue octahedra and the red, green, and blue spheres represent TiO_6, Ca, Ba, and Sr, respectively. ((a) Courtesy of H.N. Lee, Oak Ridge National Laboratory. (b) and (c) © 2005 Nature Publishing Group; reprinted by permission [2].)

These advances were first demonstrated by growing a superlattice crystal from periodically repeated $SrTiO_3$, $BaTiO_3$, and $CaTiO_3$ building blocks. The resulting crystal has sufficient mass for a full range of bulk-like neutron scattering measurements—reflectometry, diffraction, and inelastic scattering. Thus, by altering the sample preparation method to take advantage of the characterization tools, we can now synthesize new complex metal oxides with atomic-level control, and new insights can be gained into the competition between physical dimensions of nanostructures and the characteristic length scales of collective phenomena in highly correlated electronic systems.

2.2 X-RAYS AND NEUTRONS FOR DIRECTED AND SELF-ASSEMBLY

Led by Eric Kaler, formerly at University of Delaware, and Youli Li, University of California, Santa Barbara

Self-assembly driven by thermodynamics and directed self-assembly guided by external fields offer two important ways to form heterogeneous nanoscale structures. When the structures have characteristic length scales on the order of 1 to 100 nm, they are ideally examined by small-angle scattering (SAS) methods. Dynamic processes can also be probed by neutron spin echo methods. Many problems suitable for study with these methods emerge from the field of surfactant self-assembly, from probing of the structure and interaction of supramolecular assemblies of macromolecules (e.g., polymers, proteins, and nucleic acids) to examining nanoparticles self-assembled in solution or on surfaces. See Fig. 2.3 for an example using x-ray diffraction to characterize a 2-D gold nanoparticle array as it forms on the surface of a liquid droplet.

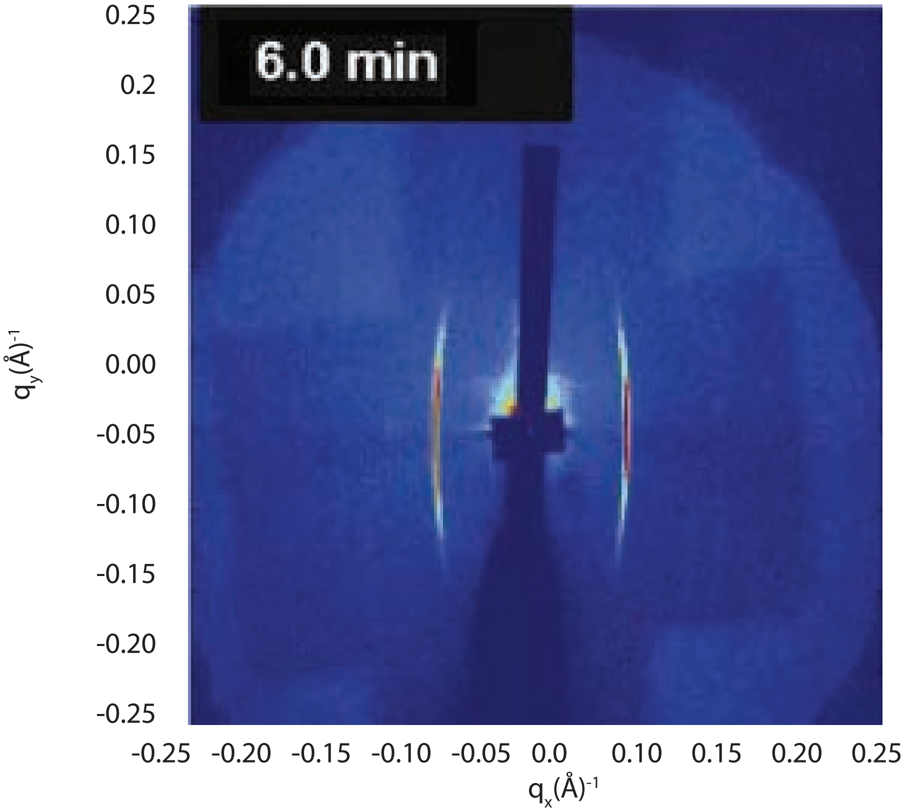


Figure 2.3. X-ray diffraction pattern from a gold nanoparticle array. (Copyright 2004 by the American Physical Society; reprinted with permission from [3].)

Understanding the nanoscale structure and interaction of these assemblies, and ultimately achieving control of the self-assembly process, has far-reaching scientific and technological implications. A variety of interactions drive the formation of hierarchical structures with length scales from a few nanometers to thousands of nanometers. Some interactions are specific (e.g., chemical bonding) while others are nonspecific (e.g., electrostatic and hydration forces).

Nature provides us with ample examples of self-assembly at work; for example, a large number of subcellular structures (e.g., the cytoskeleton) are formed and controlled through this process. The multitude of structural morphologies exhibited in nature has inspired the production of manmade nanostructured materials for a broad range of applications, including drug and gene delivery agents, nanoporous networks, and miniaturized biosensors.

Applying x-ray and neutron techniques to characterize self-assembly presents unique challenges. One common characteristic of self-assembled structures is the low degree of ordering in the material, which weakens the scattering signal. Consequently, the data quality improves tremendously when high-brilliance sources are used. In addition, the low scattering angles associated with the large length scale of the structure (1 to 100 nm) require special data collection and analysis methods. Small-angle x-ray scattering and small-angle x-ray diffraction are the most common tools used for investigating the structures of supramolecular assemblies. Small-angle neutron scattering offers the particular advantage of facile contrast variation because the scattering power of hydrogen and deuterium isotopes is dramatically different.

Another challenge in investigating the structure of supramolecular assemblies stems from the vast amount of phase space in these typically multicomponent systems. To systematically map out structures and properties is a daunting task, best tackled with parallel processing strategies. A high throughput instrument platform, incorporating automated (robotic) sample preparation in arrayed microfluidic devices and rapid data collection using microfocused x-ray and neutron beams, would dramatically accelerate the discovery of high-value structures with unique properties for a wide range of applications. To realize the potential of this strategy, it is essential that automated data processing and data mining tools be developed in tandem with instrumentation capabilities. In addition, the instruments should be capable of performing multiple structural characterizations simultaneously, for example, making x-ray or neutron and optical measurements at the same time, *in situ*, under controlled environmental conditions. Ideally, development of the high throughput multiscale characterization platforms should be carried out with active participation by researchers in the field. Once the technology is developed, general user facilities should be set up and supported at national centers to allow access by the broader community.

One example of self-assembly research is structural studies of diblock copolymers, where it is found that hexagonally packed cylinders are formed in a specific range of the diblock's fraction and Flory interaction parameters. These cylinders may orient either parallel or perpendicular to the substrate, and the degree of crystalline order is in part controlled by the solvent concentration and film thickness. Real-time grazing incidence small-angle scattering (GISAXS) studies, along with optical thickness measurements, provide a means of correlating the structure with the solvent concentration [4]. Another excellent example investigates monolayers of nanoparticles, capped with organic ligands, in the presence of ultra-thin (< 10 nm) liquid films. When the nanoparticle diameter is comparable to the solvent film thickness, the crystallinity of the monolayer is improved, regardless of the detailed solvent properties. For poor solvents, bulk nanoparticle aggregation can be induced.

Soft matter systems now being studied at the nanoscale are often hybrid assemblies, for example, nanoparticles in a polymer matrix or inorganic nanocrystals decorating organic fibrils. Such hybrid systems incorporate ordering from nanometer to micrometer length scales. The local atomic structure and associated functionality are as important to the overall properties as the long-range correlations. The systems are often sensitive to radiation and environmental factors. When fabricated into devices containing a range of buried interfaces, they are usually solution-processed. Their assembly is often directed by mechanical constraints, chemical templates, or external fields. X-ray characterization of the evolving structure of hybrid systems under processing conditions presents considerable challenges for current synchrotron x-ray facilities.

The current trend at synchrotron facilities is to optimize beam lines for a specific x-ray technique, both in instrumentation and staffing. This specialization offers advantages in terms of rapid access to standardized setups as well as access to instrumentation that is fine-tuned for specific techniques. These optimized beam lines (such as x-ray SAXS-GISAXS beam lines with *in situ* processing chambers and complementary probes, or the new nanoprobe beamline at Argonne National Laboratory) will address most of the characterization needs for soft matter nanoscience assemblies. There will continue to be a need for "general-purpose" beam lines, which provide the flexibility for researchers to develop new approaches to sample characterization. For example, efforts are underway to develop new approaches for soft matter characterization using general-purpose undulator beam lines. One project involves the study of 100 × 100 μm patterned areas of layered liquid crystals created using polymer alignment coatings scribed via atomic force microscopy (AFM). A second project involves analysis of crystal truncation rods to determine model-free electron density maps of semiconducting organic thin film interfaces.

Study of self-assembly in confined spaces could yield novel material properties and structures. 2–D confinement of macromolecules can be achieved in Langmuir monolayers (liquid-air interface), in solid-supported membranes or thin films (solid-liquid or solid-air interface), or by compressing thin films between parallel solid surfaces (solid-solid interface). In addition, controlled synthesis of nanomaterials and nanofabrication strategies provide a nanoscale interface to biosystems and allows one to probe, modify, or mimic live cells, cell components, or molecular structures—forming an emergent field of nanoenabled biology or *nanobiology.* Creation of such nanoscale architectures will enable new strategies for probing biosystems with neutrons.

Recent neutron reflectivity experiments have been successful in providing detailed density distribution profiles of adsorbed diblock polymers confined between two substrates (under good solvent conditions as a function of confinement). In combination with state-of-the-art techniques in polymerization and selective deuteration, controlled model architectures (such as polyelectrolyte brushes) can be built to elucidate the structure of complex systems at interfaces under confinement and applied shear stress. Further development of techniques such as grazing incidence diffraction could yield even more in-plane detailed structural information.

To assure future progress, there is an urgent need for sample environments that support the simultaneous interrogation of the sample by various means. This could include, for example, simultaneous small- and wide-angle scattering or simultaneous neutron, x-ray, and light scattering. The availability of these methods would allow direct observation of materials on a variety of length scales and documentation of the evolution of structure with time (kinetic processes). A second need is the ability to expose a sample to an external field during measurement. Examples include pressure, electric and magnetic fields, and shear (for simultaneous rheology, see Fig. 2.4).

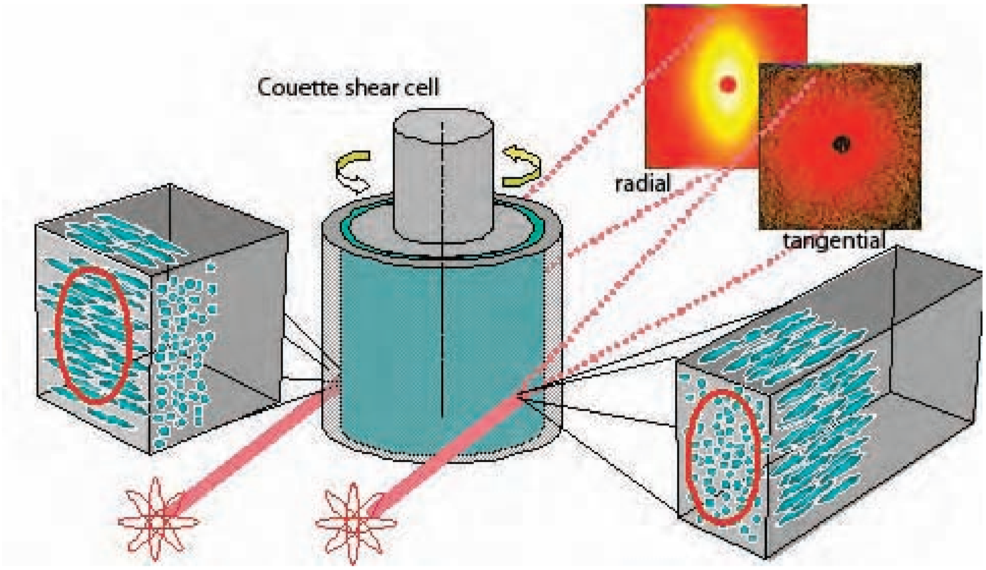


Figure 2.4. *In situ* small-angle neutron scattering measurements reveal the orientation of particles in samples undergoing shear flow, helping to elucidate the mechanism of shear thickening in suspensions of anisotropic particles. (Copyright 2005 by The Society of Rheology. All rights reserved. Used by permission from [5].)

For soft matter systems, improving signal–to-noise ratios by increasing beam flux might lead to significant radiation damage. Instead, detectors are desired that provide enhanced parallel detection, high-efficiency, and improved signal–to-noise ratios without increasing radiation damage. Using submicron-focused beams to study local structure, whether intrinsic to systems or induced by nanoscale patterning or confinement, is a challenge because the current generation of sample manipulators (goniometers) have inaccuracies (so-called spheres of confusion) between 10 and 100 μm. This is also important when doing studies of sample arrays in micron-sized cells. Possible solutions involve (1) active feedback systems (adaptive sample manipulators) optimized on the signal from fluorescent markers or some scattering feature of the sample or (2) white beam techniques that do not require sample movement. The latter approach, however, will not work for anomalous, resonant, or coherence-based techniques.

The energy range from 1 to 4 keV is crucial for the structural study of soft matter and biophysics systems because these systems often incorporate atoms with K-edges in this energy range, including Na (1.07 keV), Mg (1.3 keV), P (2.1 keV), Cl (2.8 keV), S (2.5 keV), K (3.6 keV), and Ca (4.0 keV). There are currently no dedicated x-ray scattering beam lines that cover this energy range. Vacuum ultraviolet (VUV) beam lines with ultrahigh vacuum chambers and grating monochromator optics cover the energy range below this, while hard x-ray beam lines, usually terminated by thick beryllium windows and double-crystal monochromator optics, cover higher energies. Two important techniques that require energy tuning to the absorption edges are resonant x-ray scattering and anomalous SAXS. Resonant x-ray scattering is a unique probe of orientational order in soft matter systems when the ordering occurs on a nanometer-length scale. As an example, Fig. 2.5 illustrates the nanoscale interlayer orientational correlations that can develop in tilted layered smectic C liquid-crystal phases. When the incident x-ray beam is tuned in energy to the resonant edge of one of the atoms in the core of a constituent molecule, the off-diagonal components in the tensor x-ray structure factor become significant. Orientational periodicities will then diffract x-rays and can change the

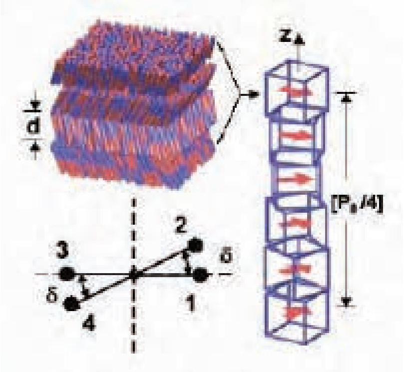


Figure 2.5 Orientational periodicities in tilted, layered liquid crystal phases. Left: a phase with a uniform in-plane modular tilt direction, which varies between layers exhibiting a 4-layer unit cell of size 1.2 nm. This unit cell helically rotates with a 1.5 mm pitch. Both periodicities can be observed by resonant x-ray scattering (Courtesy R. Pindak, Brookhaven National Laboratory.)

polarization state. An analysis of the diffracted resonant satellite peak positions, intensities, and polarization state enables a detailed structural determination of the orientational order, essential information for understanding the electro-optical behavior of these materials in devices. The technique of anomalous SAXS is important for problems in biophysics because it provides a mechanism for enhancing contrast. For example, anomalous SAXS can be used to measure the structural ordering of the counterions associated with DNA in solution, as shown in Fig. 2.6.

Another area for concerted effort is the development of software tools that can perform sophisticated analysis and modeling of scattering data from noncrystalline samples with an easy-to-use interface. The rapid advances in protein crystallography can be partially attributed to the development of such packages. However, generalized software tools are not currently available to model partially ordered or completely disordered systems, which characterize most self-assembled nanostructures. This limits the ability of nonexperts to derive maximum information from their data. The NNI can play an important role in initiating and supporting these efforts.

Finally, the issue of radiation damage should not be overlooked; it is especially important for soft matter and biological materials in microfluidic arrays. In collecting data sets of comparable signal-to-noise, it is important to know whether microfocused beams increase or reduce accumulated damage in organic systems compared with an unfocused beam. Systematic studies are required to determine the answer. Also, further studies are required to learn how to cryocool samples to reduce secondary radiation damage in a way that minimizes degradation to sample structure.

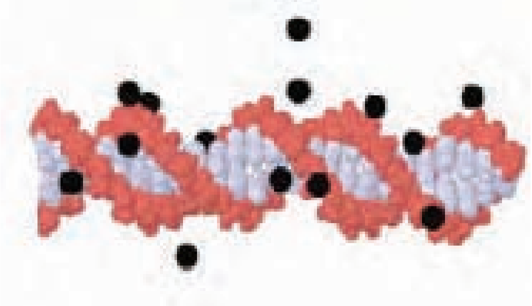


Figure 2.6. Counterions surrounding DNA in solution. The counterions can form periodic structures along their associated DNA molecules. (Reprinted with permission from [6], copyright 2003 by the American Physical Society.)

2.3 X-RAYS AND NEUTRONS FOR NOVEL PROPERTIES: EMERGING FUNCTIONALITY AT THE NANOSCALE

Led by Wayne Goodman, Texas A&M University, and Eric Fullerton, Hitachi Global Storage Technologies

The NNI defines nanotechnology as the understanding and control of matter at dimensions of 1 to 100 nanometers, where unique phenomena enable novel applications. The roots of nanotechnology may be traced to the development of bulk materials such as permanent magnets, in which the functionality is derived from a complex two-phase microstructure that is achieved through bulk processing. The current approach to nanoscience involves a close coupling of synthesis, theory, and characterization of materials at the nanoscale that allows for materials design that goes well beyond this earlier Edisonian approach. An understanding of new properties at the nanoscale and their relationship to function will lead to new applications in diverse areas such as catalysis, photovoltaics, fuel cells, membranes, adsorbants, coatings, displays, ceramics, thermoelectrics, adhesives, sensors, batteries, pharmaceuticals, and magnetic and semiconducting devices. As such, intense experimental and theoretical research activities are currently addressing the novel properties of nanostructured materials.

The physical properties of materials can be modified by confinement in one, two, or three dimensions forming 2-D thin films or surfaces, 1-D wires, and 0-D clusters and particles. In the focus session discussion of novel properties, all these classes were discussed and their importance highlighted. The research on 2-D structures is certainly the most mature, with a range of important contributions. The ability to make well-controlled quantum-well heterostructures has led to new devices that are at the heart of modern semiconductor science and technology, with applications ranging from high electron mobility transistors, to the semiconductor lasers and other optoelectronics used for optical communications, to the quantum Hall effect. An analogous revolution is currently underway in the magnetics industry due to new “quantum engineered” magnetic materials which are artificially structured at the atomic level to produce the desired magnetic properties. Spin-polarized quantum wells have been observed in metallic structures, which lead to new properties such as oscillatory coupling of two magnetic layers via a non-magnetic metallic interlayer and giant magnetoresistance (GMR). In particular, the discovery of GMR in 1988 has proven key for the field of magneto-electronics. The combination of these two disciplines where both the charge and spin of the electron are manipulated (often referred to as “spintronics”) has the potential to replace many current semiconductor and magnetic devices and provide the technology for quantum computing.

For the continued development of spintronic devices, it is essential to have detailed information on the structural, magnetic, electronic, and dynamic characteristics of the nano components of functional magnetic devices, as well as the interfacial structure between the components. Synchrotron and neutron scattering will continue to play a dominant role. By virtue of the neutron spin, spin-polarized neutron reflectivity from layered heterostructures quantitatively determines the magnetic (both the vector component and magnitude) and structural depth profile with subnanometer resolution. Lateral information on the magnetic and structural roughness as well as the domain behavior and reversal modes is determined from diffuse scattering. In the near future, it should be possible to extend these elastic scattering studies to inelastic studies to probe the excitations in two-dimensional structures. At synchrotrons, various soft x-ray resonant magneto-optical techniques have emerged that complement the information learned by neutron techniques. Resonant x-ray techniques provide element, chemical, and magnetic sensitivity via the sharp core-level resonances available in the soft x-ray range (e.g., L edges for the 3-d transition metals and M edges for rare earths). Considerable element-specific information is learned from spectroscopic techniques such as magnetic circular dichroism (MCD) and magnetic linear dichroism (MLD). These contrast mechanisms have been used to gain spatial information via various scattering and imaging techniques (e.g., Fig. 2.7). The 1 to 2 nm soft x-ray wavelengths set the spatial resolution currently achieved in scattering experiments and potentially achievable in imaging. When combined with pump-probe techniques, sub-nanosecond temporal resolution is now possible and may be extended to the picosecond time scales.

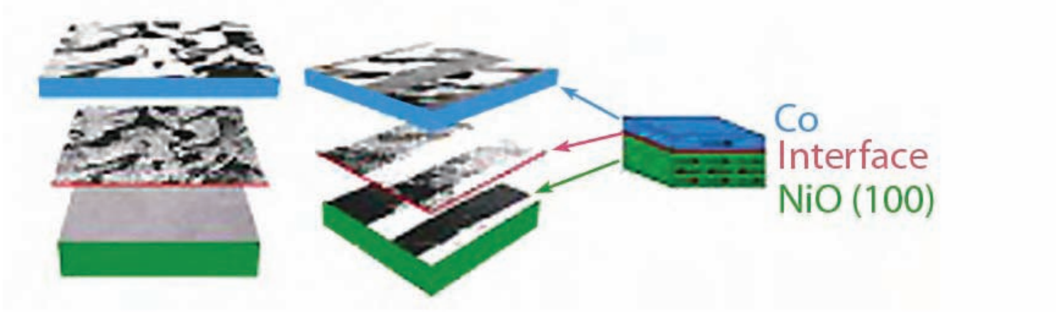


Figure 2.7. X-ray images of the interface between ferromagnetic cobalt and antiferromagnetic nickel oxide, for two different rotations of the sample with respect to the polarization of the incoming beam. The top and middle images utilize magnetic circular dichroism to image the ferromagnetic domains. The bottom images utilize magnetic linear dichroism to image the antiferromagnetic domains. (Copyright 2001 by the American Physical Society; reprinted with permission from [7].)

As nanoscience moves toward one-dimensional wires and zero-dimensional particles, the role of interfaces, interactions, and confinement will be increasingly dramatic. Advances in experimental methods together with first principle theoretical calculations promise to unravel the complexities of materials at the nanoscale, an understanding that will impact a spectrum of technologies. Real-time feedback will help drive both experiments and calculations towards a common understanding. Nanoscience is uniquely positioned because there is now an overlap of the size of the system that can be calculated with the materials that can be made and characterized. Therefore, first principle or multiscale calculations can be made of systems that are being experimentally explored, and provide stringent tests of both. This synergy may be further enhanced by focusing efforts on “standard” or ”benchmark” problems and situations where a range of theoretical and experimental techniques can be compared on well-controlled samples.

An example of this synergy can be seen in the understanding of gold (Au) clusters. By mass selection, Au clusters with atomic precision can be synthesized, and their electronic properties vary dramatically with the addition or subtraction of a single atom. These results can be compared to theoretical models and benchmark our understanding. The surprising complexity that can be observed even in this relatively simple system points towards both the challenges and opportunities of nanoscience. One example is the unique catalytic properties of nanostructured gold. Mass-selected clusters can be deposited on oxide surfaces and imaged with atomic resolution. The cluster-specific chemistry can be probed, and the nature of the interaction between the cluster and support computed with advanced theoretical methods (see Fig. 2.8). Future research efforts will emphasize the study of property–function relationships under experimental conditions realistic to the function, i.e., *in operando*. X-ray and neutron facilities provide ideal probes for *in operando* investigations at the atomic level with unprecedented temporal and spatial resolution of the structural, chemical, and electronic properties of materials at the nanometer scale.

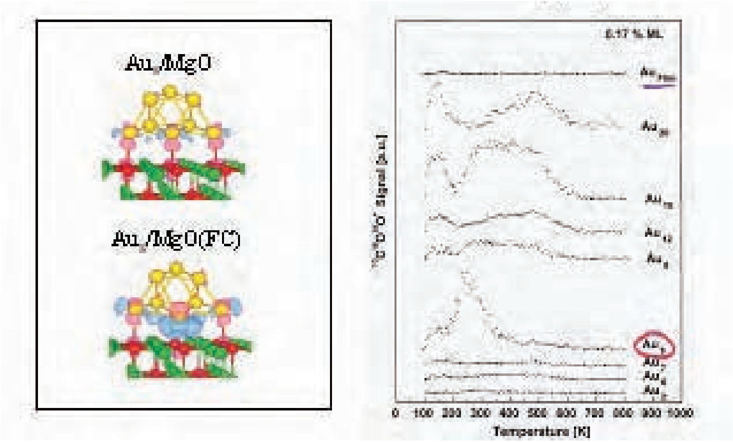


Figure 2.8. A theoretical description of the adsorption of gold on magnesium oxide, with and without an F-center defect, can be correleated with experimental measurements of the rate at which the adsorbed gold atoms oxidize carbon monoxide. (Right: from [8], copyright 2006 by Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim. Left: from [9], reprinted with permission from AAAS.)

X-rays offer unique opportunities to probe the special properties of single nanoparticles and of nanostructured materials at the atomic level. Resolution within the nanometer regime is state-of-the-art and allows structural and electronic measurements to be acquired under realistic environments. For example, recent synchrotron studies have shown the evolution of surface species using x-ray absorption near-edge spectroscopy (XANES) and x-ray photoelectron spectroscopy (XPS) during the course of a surface catalyzed reaction (Fig. 2.9).

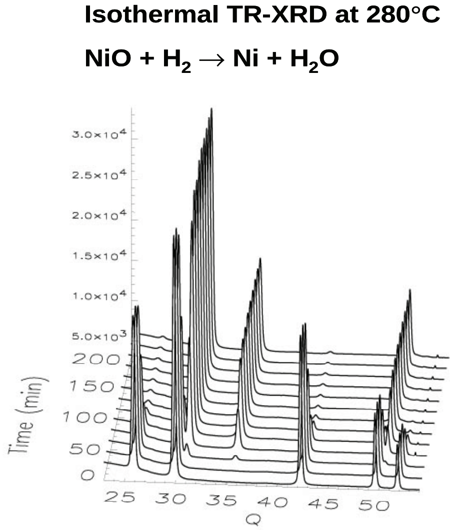


Figure 2.9. Kinetics of nickel oxide (NiO) reduction from TR-XRD. (Copyright 2002 American Chemical Society; reprinted with permission from [10]).

Structural profiling of a catalyst material under realistic reaction conditions with real-time resolution using extended x-ray absorption fine structure (EXAFS) and time-resolved x-ray diffraction (TR-XRD) has also recently been realized (Fig. 2.10). Such experimental studies matched closely with theoretical calculations promise a completely new understanding of the interplay of structure and function in materials of limited dimensionality.

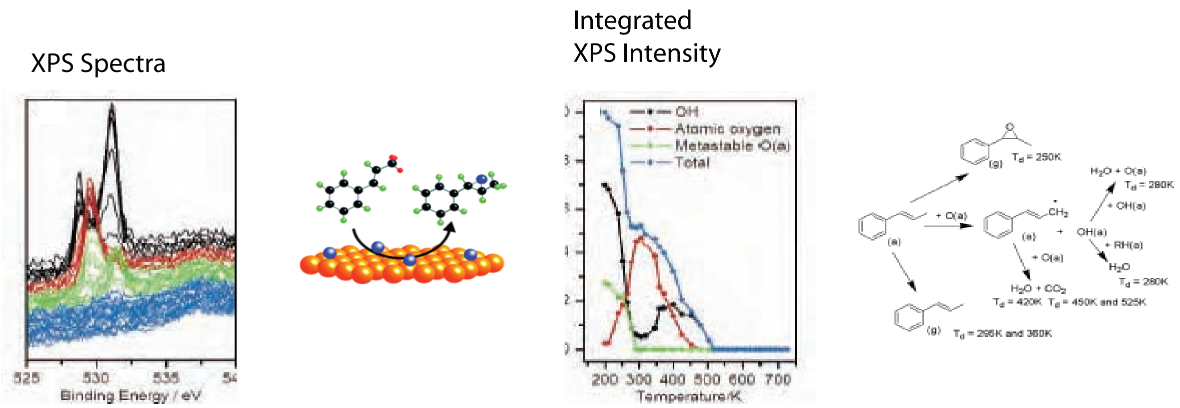


Figure 2.10. Time-resolved x-ray diffraction studies of trans-methylstyrene molecules and oxygen adsorbed on the (111) surface of copper show selective oxidation under certain conditions, pointing the way to improved catalytic processes. (Copyright 2005 American Chemical Society; reprinted with permission from [11].)

Neutrons are ideally suited for assessing the structural and chemical properties of nanostructured materials. Neutrons are highly penetrative, allowing samples to be probed *in operando* in stainless steel vessels at high pressure and temperatures. Neutrons are non-perturbing and provide atomic-level information regarding structure of nanoparticles (see Fig. 2.11) and molecular species on the surface of nanoparticles (see Fig. 2.12).

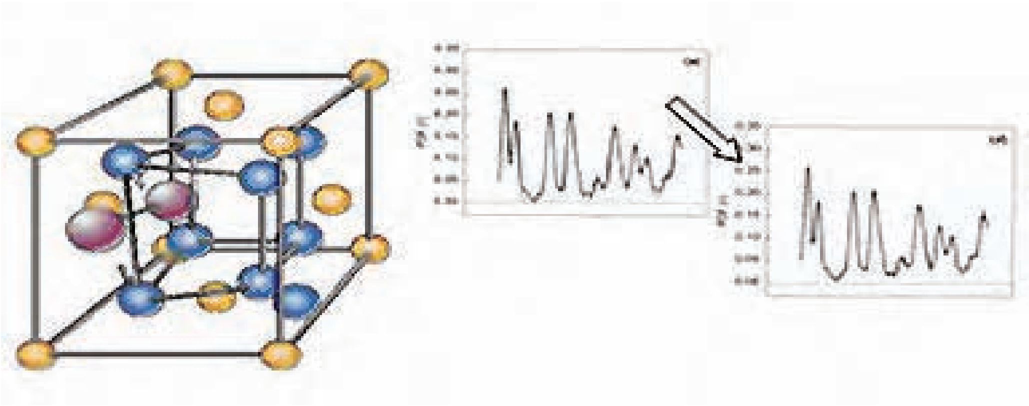


Figure 2.11. Atomic-level details of the structure of cerium oxide nanoparticles alter their efficacy in automobile catalytic converters. Left: Model of cerium oxide structure showing the interstitial location of the active oxygen sites (purple). (Copyright 2001 by Macmillan Publishers Ltd; reprinted with permission from [12].) Right: Measurement of the pair distribution function via ion scattering was combined with modeling to determine the structure. (Copyright 2000 by Elsevier Science Ltd; reprinted with permission from [13].)

With respect to assessing the unique chemical properties in and on the surface of nanostructured materials, inelastic neutron scattering (INS) can be used effectively to study the adsorption, entrainment, and reactivity of molecules and reaction of intermediate species, especially those containing hydrogen. INS studies can be performed *in situ* under relevant temperatures and pressures, and in certain situations under flow conditions, by incorporation of newly available environmental cells. INS studies can be carried out concomitantly with optical pumps and probes and thermodynamic analysis. New spectroscopic neutron instrumentation is on the horizon analogous to IR Raman spectroscopy with simultaneous structural capabilities. For inelastic measurements two orders of

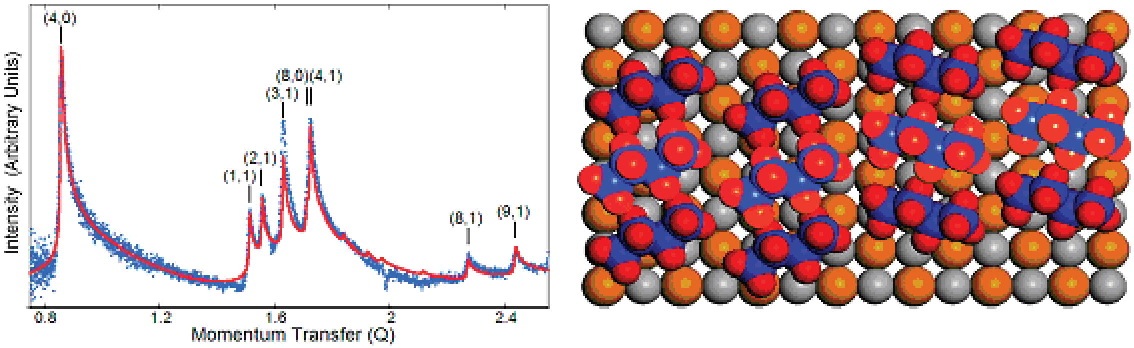


Figure 2.12. Nanoparticle film structures: Left: Neutron diffraction profile of a monolayer butane film on magnesium oxide (MgO) nanocubes. (Copyright 2006 by the American Physical Society; reprinted with permission from [14].) Right: Model showing overlayer (red and blue) with $\sqrt{2}$ by $7\sqrt{2}$ periodicity atop substrate (orange and gray). (Courtesy J. Z. Larese, Oak Ridge National Laboratory.)

magnitude higher throughput will be realized compared to the current best-in-class instrumentation. This advance in instrumentation will enable real-time studies of a wide variety of chemical and physical phenomena at the nanoscale and in nanostructured materials, including molecular motion in channels, pores, and tunnels on a time scale significantly enhanced compared to that currently available.

As increasing numbers of approaches are developed for the synthesis and self-assembly of nanoparticles, the development of functional material will be driven by the ability to characterize the physical and structural properties of a single particle, the collective response of an ensemble of interacting particle, and the properties of particles in an operating environment. For many applications such as magnetic data storage, it is hoped that self organization will allow progress in densities well beyond what is achievable by conventional lithography. While chemically synthesized, self-organized nanocrystals are one of the more exciting areas in magnetism, their macroscopic properties are often more complex than first anticipated. Exploiting these materials will require combining synthesis, characterization, and modeling to arrive at a more detailed understanding. It is here that synchrotron radiation and neutron techniques will have an increasingly important role. For magnetic nanoparticles, both resonant x-ray and neutron scattering have been able to characterize the average magnetic moment, electronic, and chemical state of the particles via spectroscopies (MCD, MLD), and the relative surface and magnetic order and the relative particle orientations via spin-polarized small-angle neutron scattering (SANS) and resonant x-ray scattering, as shown in Fig. 2.13.

This example shows resonant small-angle neutron scattering from a self- assembled array of 9 nm cobalt (Co) particle. The scans were measured at room temperature where the particles are superparamagnetic and the magnetization of the particles is expected to randomly fluctuate due to thermal energy. However, for the ε-Co sample the magnetic x-ray scattering indicates that the magnetization directions of adjunct particles are highly correlated, even when highly thermally activated.

The ability to measure the magnetic response at the inter-particle spacing is a particular strength of x-ray and neutron techniques. A challenge will be the equivalent measurement for single nanoparticles. The importance of this will be to separate the roles of particle interactions and particle-to-particle variations for understanding the response of the composite. Where this is not possible, it will put increasing demands on the synthesis of particle arrays with limited particle-to-particle variations.

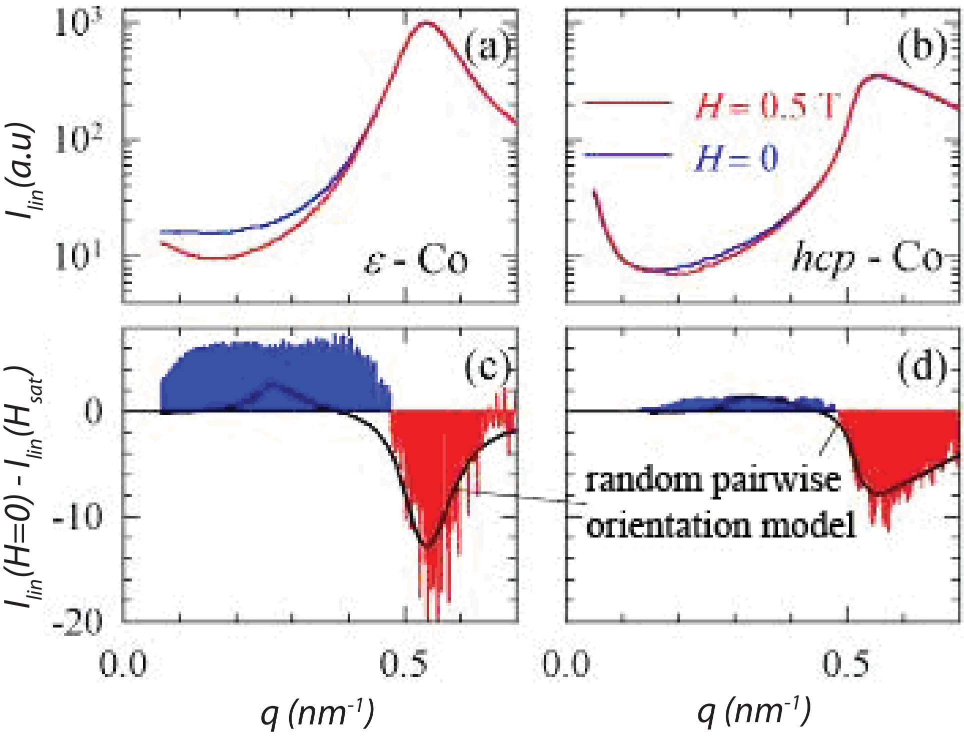


Figure 2.13. Resonant small-angle scattering from a self assembled array of 9 nm cobalt (Co) particle. (Copyright 2005 by the American Physical Society; reprinted with permission from [15].)

An exciting area of nanoscience is the expectation of increased complexity or emergent behavior as one builds materials from the nanoscale. That is, local interactions give rise to higher-level, large-scale patterns of behavior that are not readily expected. This phenomenon can arise from competing interactions among multiple phases with similar energies. Such complex behavior can be observed in nanostructure materials with competing interactions. Figure 2.14 shows the domain pattern of a magnetic multilayer with perpendicular anisotropy and antiferromagnetic coupling between the layers. The dipole fields tend to favor ferromagnetic domains while the interlayer coupling favors antiferromagnetic domains. The resulting domain structure has surprising long-range order and complexity. Such behavior is observed in the complex oxide materials such as high-technetium (Tc) cuprates, the colossal magnetoresistance (CMR) manganites and cobalites, and multiferroic materials.

In such materials one has interplay of the spin, charge, and lattice degree of freedom, and it is common to see the spontaneous phase separation in various magnetic phases on the nanometer scale. A question arises whether this phase separation is linked to local structural variations (intrinsic vs. extrinsic mechanisms) and whether this behavior can be controlled and exploited. This is a particularly fascinating question as one reduces the dimensionality of the material. In this field, x-ray and neutrons are clearly the techniques of choice because they can measure both the magnetic and structural heterogeneity on the nanometer scale via small angle scattering, microprobe techniques, and imaging.

Studies combining x-rays and neutrons can clearly provide a new level of clarity and understanding regarding the delicate interplay between the atomic-level structure of materials at the nanoscale and their corresponding properties. Advances currently realized at our national facilities promise new

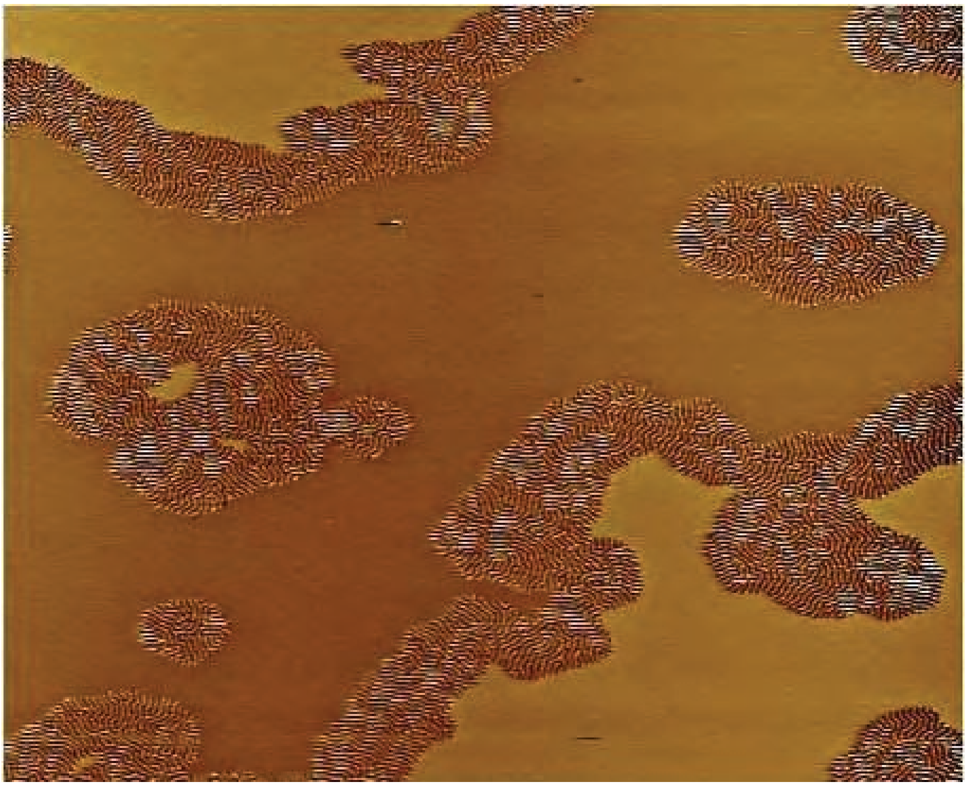


Figure 2.14. Two-phase domain behavior of a magnetic multilayer (Courtesy E. Fullerton, University of California, San Diego.)

capabilities that will allow measurements of physical and electronic structure together with chemical dynamics in real time and under realistic conditions. These insights will unquestionably lead to an array of materials with new functionalities and provide the impetus for new technologies.

2.4 ADVANCED X-RAY AND NEUTRON TECHNIQUES

Led by Roland Gähler, Institut Laue-Langevin; Wenbing Yun, Xradia, Inc.; Gabrielle Long, Advanced Photon Source, Argonne National Laboratory; and Dan Neumann, National Institute of Standards and Technology

X-rays and neutrons have intrinsic atomic resolution, which, combined with modern synchrotron and advanced neutron facilities, enables powerful new nanoscience-specific techniques. Each probe provides unique insights to the science, and they are complementary in investigations of the complex phenomena underpinning this field. For example, neutrons are uniquely sensitive to the dynamics of materials. As described subsequently, with neutron techniques it is therefore possible to uniquely clarify the interrelationship between atomic structural dynamics, local crystal structure, particle size, the influence of low-atomic-number elements, and magnetic properties. Not only can neutrons provide information on nanoscale materials, but often the measurements can be taken nondestructively, *in situ*, or below the sample surface. To facilitate the application of neutron methods to nanoscale materials, emerging neutron methods that efficiently provide intense neutron beams for small sample volumes are essential. These methods allow characterization of often precious nanomaterial samples, as well as combinatorial measurements of nanomaterials libraries.

Ultrabrilliant third- and fourth-generation synchrotron x-ray facilities are similarly poised to revolutionize our understanding of nanoscale materials. These facilities have the inherent brilliance (photons/s/mm^2/mrad^2/$\Delta\lambda$) to nondestructively study very small sample volumes, with unique sensitivity to elemental distributions, chemistry, and atomic structure. Again, measurements can often be made nondestructively, *in situ*, and in 3-D. With intense x-ray beams, it can also be practical to study nanoscale properties in real time. The emergence of high-performance x-ray optics and novel new imaging techniques will enable exciting studies of single nanoscale particles and the investigation of heterogeneous samples with 3-D nanoscale structure. This information is certain to revolutionize our understanding of nanoscale materials.

Advances in X-ray Techniques

X-ray based techniques can uniquely address many key questions of nanoscale science.What are the elements? How are they arranged? What is their chemistry? Where are their defects? How do properties change within particles and how do all the above change as a function of particle size and environment? X-ray crystallography has long played an essential role in materials science and molecular biology, and x-ray spectroscopy has similarly guided chemistry and our understanding of catalysis. Nanoscience, however, requires that x-ray characterization techniques be extended to small samples, samples with weak signals, or samples with nanoscale inhomogeneous structures. Although existing x-ray instruments have already contributed to the rapid advancement of nanoscience and nanotechnology, limitations in terms of resolution, sensitivity, and accuracy are widely recognized. Nanometer-scale spatial resolving power added to x-ray spectroscopy, diffraction, time resolved scattering, and imaging is critically needed for nanoscience research, ranging from assisting in the discovery of functional nanomaterials and devices to controlling synthesis and manufacturing processes.

X-ray imaging techniques, with nanoscale resolution, will have a major impact on nanoscale research by enabling fundamentally new ways of characterizing nanoscale materials. Various contrast mechanisms can be used to obtain detailed 3-D characterization of composition, chemistry, texture, structure, and defect distributions near and within nanoscale features. This can often be carried out nondestructively with minimal sample preparation. For example, using nanoparticles as markers, x-ray 3-D cryo-tomography with nanometer resolution will enable the study of many important biological processes and drug discovery, and complement optical and electron microscopy techniques. Nondestructive 3-D tomography with nanometer resolution will play an important role in the development and manufacturing of future-generation nanostructured high-performance electronic devices and nanocomposite materials of desired chemical, mechanical, and materials properties. This information can be directly connected to functional properties and can be compared to, or used as input for, theoretical modeling.

Currently, there are two attractive approaches to high-resolution x-ray imaging: one that uses a high-resolution lens and another that does not use a lens but requires coherent illumination. The image in Fig. 2.15 is obtained using the lens approach [16], while the images in Fig. 2.16 are obtained using lensless coherent illumination. In recent years, both imaging techniques have demonstrated rapidly improving resolution. While the lens-based approach requires a high-performance objective much like a standard optical microscope, it does not require a source with a high degree of coherence. In fact, using a laboratory x-ray source, sub-50-nm resolution 3-D imaging has been achieved by Xradia, Inc.

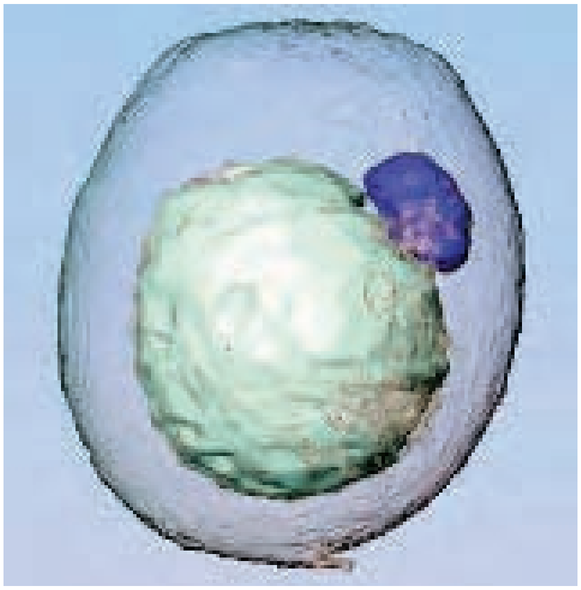


Figure 2.15. Three-dimensional x-ray tomography allows the structure of a rapidly frozen, fully hydrated yeast cell to be determined with 60 nanometer resolution. The outer surface of the cell has been rendered translucently to reveal the internal organelles. The compact blue object is the cell nucleus. (Courtesy C. Larabell, University of California, San Francisco.)

The lensless alternative does not require an x-ray lens but does require a high-brilliance x-ray source such as a fourth-generation synchrotron source.This approach depends critically on ultra-coherent x-ray sources such as the so-called fourth generation x-ray synchrotrons sources currently under development in the United States and worldwide. As shown in Fig. 2.16, the diffraction pattern from a micron-sized gold particle can be used to reconstruct the real-space image of the particle. Critically, this method provides information both on the interior of the object and on defects within the object.

The image was obtained by first collecting projection images over a large angular range using a transmission x-ray microscope and then reconstructing the 3-D view via a computer. With improvement in x-ray optics, spatial resolution is expected to reach about 10 nm within the next few years and ultimately to approach 1 nm. Using nanoparticles such as quantum dots as markers, the tomography imaging technique will enable the study of many important biological processes and also drug discovery.

A new x-ray microscopy method called x-ray reflection interfacial microscopy (XRIM) has recently demonstrated atomic-scale resolution [19]. Using this technique, a change in step height on a crystal surface by a single unit cell (0.65 nm) was clearly imaged. The resolution in the other two directions is currently limited to about 200 nm but can be improved substantially with higher resolution x-ray optics. It is important to note that a diffracted or reflected beam is used in XRIM instead of the usual transmitted beam. Although other techniques do exist for imaging unit-cell surface steps (including reflection electron microscopy and scanning probe microscopies) the XRIM technique opens many new exciting applications for *in situ* studyies of surfaces or interfaces in a range of environments.

For the past decades x-ray spatial resolution (imaging and microbeam) has improved by a factor of two every few years. This revolution has been driven by the development of ultra-intense synchrotron x-ray sources and by the emergence of new fabrication techniques for x-ray optics. It is crucial

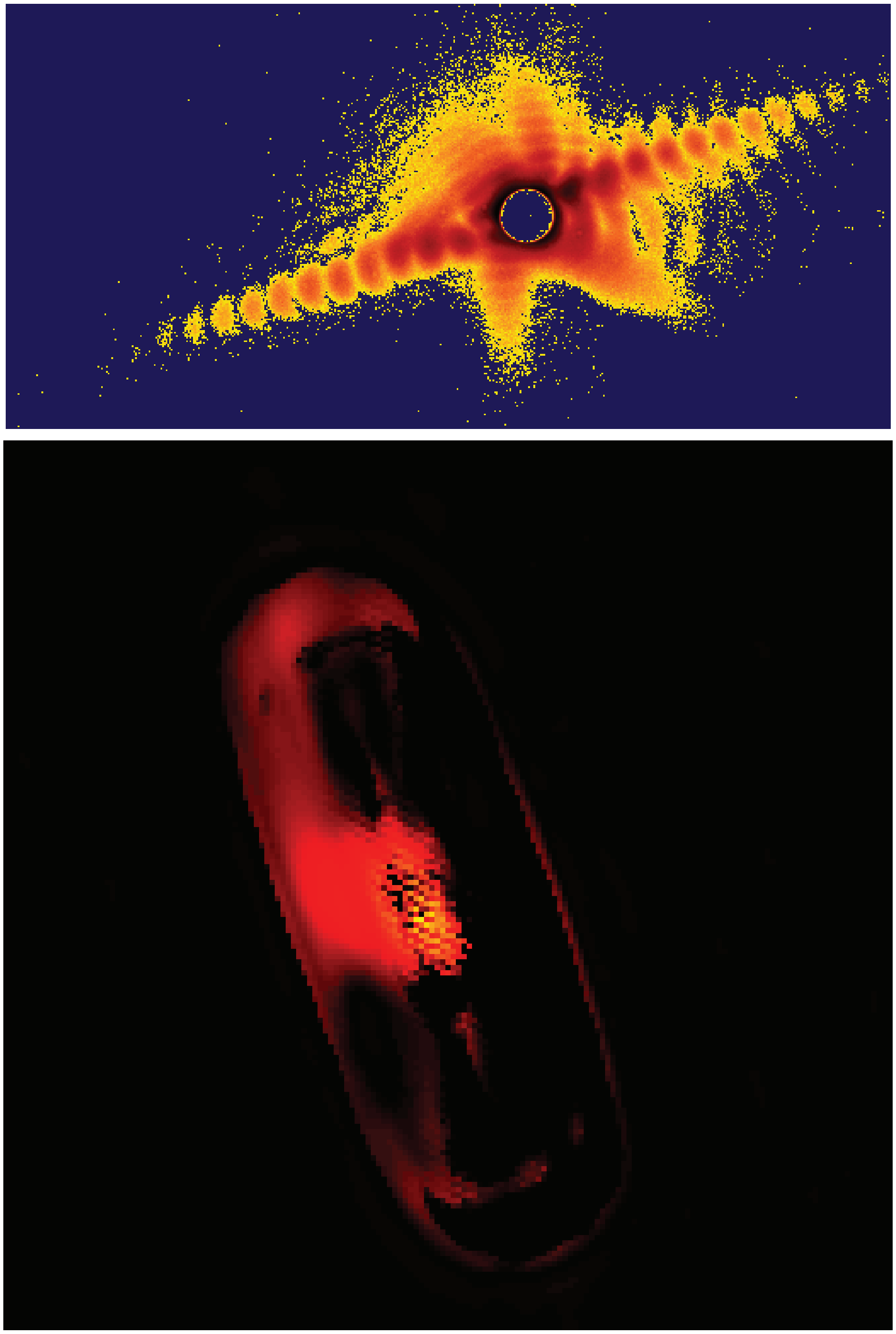


Figure 2.16. Lensless imaging offers a way to convert x-ray diffraction data (top) into real-space images (bottom) of small samples. (Copyright 2001 and 2003 by the American Physical Society; reprinted with permission from [17,18].)

to sustain this remarkable progress and bring x-ray resolution down to 1 to 2 nm—more than an order of magnitude further improvement. This will extend x-ray imaging and microbeam techniques to single nanoparticles in most materials systems and will allow for characterization of nanoscale inhomogeneities in bulk materials and intermediate-size particles.

Achieving this resolution will require revolutionary new tools and new techniques need together with evolutionary improvement of existing techniques. A straightforward extrapolation of recent progress in x-ray optics (Fig. 2.17) predicts that hard x-ray imaging and/or probing resolution will soon approach 10 nm; soft x-ray focusing has already reached this near-term goal. This extrapolation suggests that the 1 to 2 nm resolution goal may be achievable within 10 to 20 years.

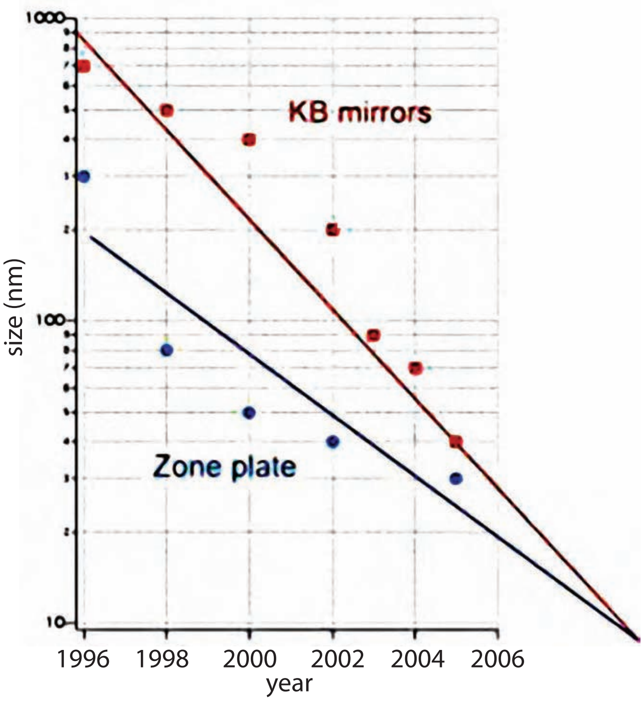


Figure 2.17. Hard x-ray spatial resolution has improved by about a factor of 2 every 2 years for the last decade. At this rate, spatial resolution below 10 nm should be achieved around 2008 and spatial resolution around 1 nm around 2015. The ability to focus x-rays to small beams will allow for a range of powerful characterization methods to be applied to individual nano particles or to nanoscale volumes in heterogenous materials. Imaging methods will allow researchers to nondestructively identify sample volumes of interest within larger samples for additional characterization. KB = Kirkpatrick-Baez. (Courtesy G.E. Ice, Oak Ridge National Laboratory.)

At least three approaches have emerged for producing scanning x-ray probes: zone plates, compound refractive optics, and Kirkpatrick-Baez (KB) optics. All three appear poised to produce beams below 10 nm in the next 2 to 4 years. Projection full-field imaging, or full-field microscopy, has also been demonstrated with resolution ~10 nm; this allows for both 2-D radiography and 3-D tomography on relevant length scales for nanoscale materials. In addition, coherent diffraction imaging methods offer the promise of high 3-D spatial resolution of isolated nanoscale particles with sensitivity to 3-D structure morphology and defects.

Advances in Neutron Techniques

The coherence length of neutron beams (typically between 1 and 100 nm) makes them uniquely suited to probing both the internal structure of nanoparticles and molecules attached to their surface or entrained within their internal volume, and space–time correlations of ensembles of such systems. Identifying the relationship between structure and dynamics over a wide range of distance and time scales is crucial to understanding and predicting the pathways leading from self-assembly of nanoparticles to the formation of functional units. Moreover, neutrons can distinguish between individual motions and correlated motions in an ensemble of particles, particularly for large molecular units such as emulsions, polymers, and biological molecules.

To completely cover the distance and time scales relevant to nanoscience, new developments are required in focusing methodologies, small-angle neutron scattering techniques, time-stamping methods, and other emerging methods. These are discussed in the following subsections.

Focusing Methodologies

Neutron sources have intrinsically low brilliance compared to x-ray sources; even next-generation neutron sources will provide a brilliance 14 orders of magnitude lower than modern synchrotron sources (and 17 orders of magnitude less than is expected at future free electron lasers). Therefore, advances in neutron techniques are primarily aimed at making the most efficient use of the available flux, either by focusing or by decoupling the relation between spatial (or time) resolution and beam divergence imposed by phase-space considerations. This is especially important in studying nanostructures given the relatively small sample volume of interest.

Emerging neutron focusing methods will extend neutron measurements to much smaller sample volumes than previously possible. They will also improve the angular resolution of SANS methods, providing a means of extending the sensitivity of the technique to object sizes of 1000 nm or more. Neutron beams can be focused in space using reflection from mirrors (nondispersive) or refraction through material or magnetic lenses (dispersive). Neutron focusing with Kirkpatrick-Baez supermirrors approaches the theoretical limit set by the available neutron source brilliance. For small samples this can greatly increase the flux at the sample compared with traditional beam-guided optics. For example, with a clearance of about 0.25 m between sample and neutron optics, focusing optics provide an intensity gain of more than 100 for neutron beams less than 200 μm × 200 μm. Currently, beam dimensions of less than 100 μm are achievable. In the future, nested arrangements of KB mirrors will allow collection of a wider range of source divergences, leading to even more intense micron-sized beams. This improved flux density for small beams is essential to achieve adequate signal and the best signal-to-noise for small sample volumes. These beams will enable the range of *in situ* measurements to be extended to higher limits of temperature, pressure, and magnetic field.

Compound refractive lenses (CRLs) also show promise for focusing neutron beams, especially for SANS experiments; however, neutron microscopes employing CRLs are currently limited to resolving structures larger than 1 μm.

Magnetic lenses are also refractive in nature but have the advantage that there is no material in the beam path, so they do not suffer from parasitic scattering. Moreover, their transmission properties can be readily tuned by modifying the magnetic field arrangements: a sextupole magnetic lens provides excellent focusing with moderate polarization, while a quadrupole lens acts as a spin filter and collimator with very high neutron polarization. A combination of magnetic lenses provides a means of extending the spatial range of SANS measurements from 100 nm to about 1 μm and performing polarized neutron SANS measurements to image the magnetization in assemblies of magnetic nanoparticles.

Extension of SANS Measurements

Polarized beams have an added advantage for SANS measurements of polymers or other predominantly hydrogenous materials. Analysis of the spin polarization after scattering allows rejection of the enormous incoherent background scattering from hydrogen, which might otherwise dominate the signal. New techniques for dynamically polarizing the hydrogen atoms in hydrogenous samples can increase the sensitivity by further orders of magnitude. Essentially, when the neutron and proton spins are parallel, the coherent cross section (i.e., the intensity of the SANS signal) is increased by nearly a factor of 10, and the incoherent cross section (the background signal) is reduced to zero. Furthermore, the spin labeling of certain regions of a protein, nucleic acid, or polymer using electron paramagnetic resonance techniques will allow SANS measurements to "see" selected components. Dynamic polarization has traditionally been achieved at low temperature (~ 1°K) and high magnetic fields (~ 5 T). New methods using microwave induction enable the technique to be applied in biologically relevant samples in solution at ambient temperature and fairly low fields (~ 0.3 T). The combination of polarization and focusing properties of magnetic lenses also makes them candidates for pretailoring neutron beams for the novel spin echo instruments under development for nanometric surface structural and dynamical measurements.

Filling the Time Gap

The number of precessions that a neutron makes in a uniform magnetic field is a sensitive measure of the integrated field that the neutron traverses. This is the basis of neutron spin echo (NSE) techniques. Neutron spin echo techniques take advantage of this sensitivity to accurately determine energy change, angular deviation, or both after scattering. This translates to measurements of longer correlation distances and times than would be possible otherwise. Since each individual neutron carries its own spin label, the sensitivity of the technique is independent of the incident beam collimation or energy band width. Large flux increases compared with standard measurements are theoretically possible by using divergent beams with large energy band widths. Applied to SANS, the technique can extend measured correlation distances from ~100 nm to micrometers. Alternatively, standard SANS instruments equipped with sample modulation techniques can be used to measure the dynamics of nanometer-scale structures in the formerly inaccessible time range between 10^{-6} and 10^{-3} s. These pulse-probe measurements, in which the sample is subjected to a frequency modulation up to the 100 kHz range, will enable measurements of myriad phenomena including conformal changes in membrane proteins under ionic or light stimulation, nanostructure formation in ferrofluids, vortex dynamics in nanomagnets, and the response of complex fluids to stress or shear.

Applied to neutron reflectometry, neutron spin echo techniques promise simultaneous measurements of in-surface correlation lengths in the range from 10 nm to 1000 nm and correlation times in the range from picoseconds to microseconds. This will open the door to a time domain particularly relevant to processes in polymer and biological membranes, including fusion and transport mechanisms, shear mechanisms, micelle formation, assembly and folding of proteins, and transcription of nucleic acids.

For pulsed neutron facilities, which use time-of-flight techniques to determine energy or wavelength, novel magnetic techniques are being developed to focus a wide range of wavelengths in time, in theory providing order of magnitude gains in flux on sample. Increased beam fluxes and requirements for better resolution in time and space demand detector and data acquisition systems with corresponding performance improvements.

Future Directions

The techniques under development described in the previous section are certain to provide critical new capabilities for nanoscience research in the near future, in particular when combined with a next-generation source such as the DOE Spallation Neutron Source at Oak Ridge National Laboratory. Here we describe briefly some other, less mature, concepts that could dramatically extend the horizons of neutron scattering techniques in the longer term.

Boron Capture and Other Novel Drug Delivery Therapies. Recent progress in nanomedicine provides methods for functionalizing nanoparticles such that they are preferentially taken up by cancer cells. These methods can be used to image tumors or deliver fatal drugs (or "killer particles") which would destroy the tumor but leave the surrounding tissue in tact. Targeting methods could also be used as a nonpoisonous carrier to deliver boron particles to tumors; under controlled slow neutron irradiation, this would produce short-ranged lithium and alpha particles that cause significant damage in cells. One advantage of this method is that the same particles can be used to image the progress of the disease using advanced radiography methods.

Phase Space Manipulation. All the neutron optical components mentioned in the previous section obey Liouville's theorem—the density of neutrons in position/divergence phase space is maintained at constant temperature. The phase space density increases as the temperature decreases, however. Cooling the neutron spectrum from 300 °K to 4 °K (in a cryogenic moderator) increases the phase space density by a factor of 600. Doppler shifting back to cold or even thermal energies (using moving crystals or mirrors) can significantly increase neutron fluxes.

Neutron Imaging. High-resolution neutron radiography (NR) and tomography (NT) will become excellent imaging tools for nanoscience if suitable advances in neutron flux, detectors, collimators, and focusing optics are achieved. Just as in computer-aided x-ray tomography (known in medicine as CAT scan), neutron tomography generates cross-sectional images of an object from transmission data obtained by passing a beam of neutrons through the object from many different directions. Neutron tomography allows for nondestructive imaging of an object and can also be used to image objects buried deep within a container (e.g., a metal casing or ceramic enclosure), fluid flows, gas percolation, etc. By taking advantage of the large (wavelength-dependent) absorption cross section of certain materials, and of resonant absorption in special cases, NR and NT can often be far superior to x-rays tomography. Finally, both inelastic imaging and magnetic imaging could be used to explore energy-dispersive materials or magnetic materials.

Significant opportunities in neutron tomography and radiography exist in several areas:

- NT and NR phase contract techniques maybe used to measure distribution of nanoparticulates in polymer films, gels, and fluids.
- NT and NR may be used as a noninvasive diagnostic clinical tool (e.g., to examine the distribution of neutron-absorbing drug delivery systems *in vivo*, potentially for imaging of the capillary network within human lungs, dental and bone implants and repairs, and to determine the integrity of marrow within bones. (In some of these examples, neutron irradiation could be used in tandem with NT as a part of a therapeutic regime (modified neutron boron capture therapy.)
- NT and NR may be used to study hydrogen, water, hydrocarbon content, or movement/ percolation within nanometer-scale particles including metals, ceramics, operating catalyst beds, membranes, and bioorganisms.

- High-energy (eV range) NR and NT may be used to image buried interfaces in a variety of massive structures, fluid flow in encased or buried channels, etc.
- Polarized NT may be used to examine magnetic nanomaterials, ferrofluids, and magnetic particles undergoing laminar and viscous flow, as well as the response of materials under intense electric and magnetic fields.
- The pulsed nature of spallation sources can be exploited to produce time-sliced images of a variety of physical processes that may be stimulated by pulsed magnetic and electric fields, as well as optically pumped.
- Neutron holography has been demonstrated using both the internal source and the internal detector methods. New approaches to holography using time-modulation techniques show promise for direct imaging of biological and magnetic structures with atomic resolution.

Neutron Magnetic Resonance. Magnetic resonance techniques use an external magnetic field to split the spin states of a system, and then use electromagnetic radiation to excite a resonance between these two states. Typically two systems are used: unpaired electrons in molecules (electron paramagnetic resonance, or EPR) and the nuclear spin states of nuclei (nuclear magnetic resonance, or NMR). Neutrons could also be used to induce transitions between the spin states and hence offer some distinct advantages. Because neutrons interact with the spins through a different coupling mechanism than the electromagnetic-radiation-based probes, transitions that are forbidden by the electromagnetic interaction selection rules can be observed using neutrons. Furthermore, electromagnetic-based investigations of systems with large numbers of conduction electrons suffer from limited penetration depths. Neutrons in general do not have this restriction and thus the entire sample can be probed. As a magnetic field is applied to an unpaired electron the splitting of the energy levels is 0.116 meV/T. For sufficient resolution, fields greater than 30 T and resolutions on the order of 1 μeV would be required. Neutron probe EPR will be particularly useful for examining biological systems, including biomaterials, isolated biomolecules, and free radicals in intact tissues and organisms.

Evanescent Waves and Neutron Nanoguides. Under suitable conditions of the refractive index, (i.e., for certain material combinations) neutrons can be coupled into, and transmitted to the edge of thin layers with nanometer spacing. Hence, the layer system acts as a nanometer-sized coherent source that could be used for numerous applications including phase imaging and microdiffraction if sufficient intensity could be achieved. Moreover, the evanescent wave traveling close to the surface is a sensitive probe of near-surface properties and can be used to characterize lateral structures in thin films and membranes.

Because complex nanostructures are typically not long-range ordered, many unique atomic positions need to be determined to describe them. Standard crystallography cannot describe the structure of discrete nanoparticles or disordered assemblies of particles. This is in essence the “nanostructure” problem. As a result, complete characterization of a nanosystem will require a combination of information from multiple techniques. As an additional challenge, to understand many nanoscale phenomena and the synthesis of nanoscale structures, it is essential that these systems be characterized during synthesis or processing (i.e., *in situ*), often with demanding sample environments. For example, the assembly of nanocomposites for electronic, magnetic, and photonic devices can take place far from equilibrium. Control of the process requires a thorough understanding of the kinetics and requires measurement of the structure *in situ* with subnanometer resolution and in real time.

Examples of current tools that are being used to study nanostructures with *in situ* environments and in real time include x-ray-excited optical luminescence (XEOL), soft-x-ray photoemission electron microscopy (PEEM), grazing-incidence small-angle x-ray scattering (GISAXS), and coherent diffraction (or "lensless imaging"). X-ray-excited optical luminescence is of interest because nanostructured materials emit light where their bulk counterparts typically do not, and time-resolved XEOL reveals the origin of this luminescence. Time-resolved PEEM has been used to follow domain nucleation and growth within nickel ferrite (NiFe) nanodots as a function of a time-dependent field. The time-resolved GISAXS makes use of waveguide geometry to enhance the incident and scattered signal in a submonolayer of, for example, gold nanoparticles within a polymer (Fig. 2.18), thereby enabling the study of the kinetics of nanoassembly during fabrication of nanowires.

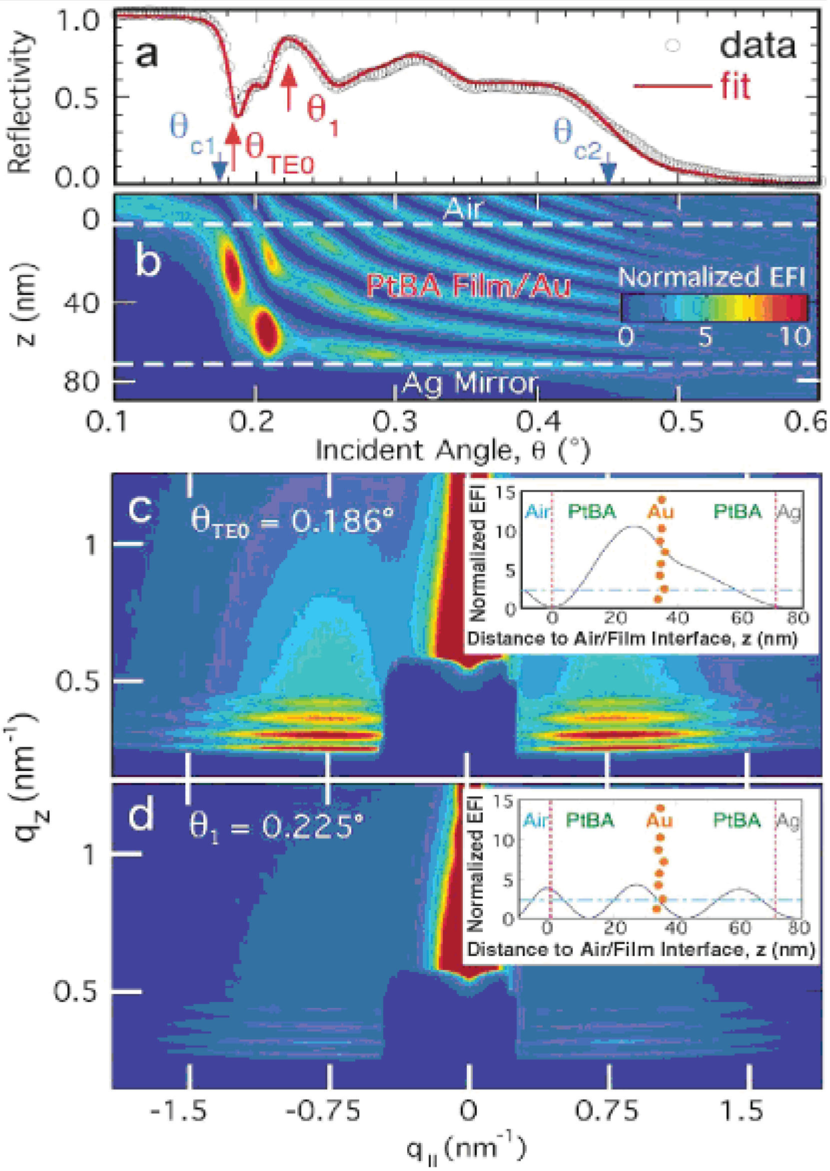


Figure 2.18. Example of the self-assembly of gold nanoparticles in a polymer matrix [20]. Normalized 2-D GISAXS measured at the first resonance condition (TE0 mode) and at off-resonance condition. The insets depict the corresponding calculated electric field intensity distribution in the film. The strong specular reflections are blocked with a beam stop. Time-evolution of GISAXS patterns, taken with resonance-enhanced x-rays, yields in-plane and out-of-plane diffusion constants. (Copyright 2005 by the American Physical Society; reprinted with permission from [18].)

Surface x-ray scattering is a unique tool to characterize the surface and the subsurface regions that dominate the energetics of small structures. Examples are vacancy formation in thin metal films (invisible to STM) and nanocrystals.

Future needs in these areas include: better focusing techniques, larger sample volumes, higher pressures, and further improvements in accuracy, precision, and application of multiple simultaneous techniques. For pressure anvils, 10-carat diamond crystals have been fabricated; the future goal is 100 carats, with custom shaping and embedded probes.

Unique sample environments also enable neutron measurements of confined liquids, such as quantum liquids in nanoporous media and on surfaces. Future goals include studying the impact of confinement on superfluidity and the structure of ^{4}Helium on and in nanotubes. Models indicate that confinement causes the formation of nanoscale droplets within the liquid helium.

Examples where neutron scattering measurements under high pressures are being applied to meet challenges in nanoscience include the following:

- hydrogen-rich clathrates, structures which contain the largest amount of hydrogen
- stability and transformation mechanisms in ZnS nanowires, for making and recovering new materials
- micromineralogy and nanomineralogy, to observe new materials in meteorites
- structure–property relations in biological structures under pressure, e.g., dynamics of model heme compounds
- viability of microbes under pressure, for studies of microbial evolution and adaptation

As the sizes of the x-ray beam reach 1 to 10 nm with a coherent flux of ~10^{15}/s/0.1% bw at 1 to 10 keV, there is the potential to revolutionize nanocharacterization: diffraction, scattering, x-ray absorption fine structure (XAFS), holography, tomography, and coherent diffraction. In the future, x-ray reflectivity and surface crystallography measurements will be improved by new detectors that have faster readout, larger dynamic range, and better energy resolution.

Many of today's neutron methods are well-suited to following the structure and dynamics of materials on the nanoscale; however, there is substantial room for improvement in, e.g., devices for manipulating neutron beams, advanced instrumentation that incorporates sophisticated sample environments, and powerful, easy-to-use software for data analysis.

In addition, deducing structural and dynamic properties by combining data from various techniques will require the development of a robust data management, analysis, modeling, and visualization infrastructure with standard formats, modeling, and simulation capability, for self-consistent optimization.

Using the atomic pair distribution function method, and measuring total diffraction ("underneath the Bragg peaks"), significant progress is being made in medium-range structure determination, e.g., on nanoparticles used in the chemical industry. Dynamic PDF determinations by means of inelastic neutron scattering offer an opportunity for measuring the dynamics of nanostructured materials, e.g., in relaxor ferroelectrics. With improved source intensity and brightness, better detectors, and improvements in data quality, it will becomes possible to extract more structural information in the 0.05 to 5 nm range.

Combinations of neutron scattering techniques can also provide unique information on phase transformations and deformation in bulk materials at the nanoscale. For instance, metallic glasses containing nanoscale crystallites exhibit unconventional properties and different deformation mechanisms that are expected for nanostructured materials. Future experimental capability includes measuring scattering data over multiple length scales, and simultaneously perfoming differential scanning calorimetry, dilatometry, or transport measurements, all while applying heat, mechanical loading, and electric or magnetic fields.

2.5 MULTISCALE THEORY, MODELING, AND EXPERIMENT

Led by Grant Smith, University of Utah, and Philip Pincus, University of California, Santa Barbara

Nanosystems are intimately intertwined with a spectrum of length and time scales. Therefore, the envisioned revolution in nanotechnology depends on a vastly improved understanding of physical phenomena centered on the nanometer length scale and the nanosecond time scale but operative at much shorter and longer scales. Progress in intelligent and efficient exploitation of length- and time-scale hierarchies in nanostructure materials relies on the development of both computational and experimental probes that are specifically designed to interrogate on multiple length and time scales. Furthermore, the physics- and chemistry-based multiscale models that will play a central role in the rational design of nanostructures with desired novel behavior, response, and properties can only be developed and validated through interdisciplinary, collaborative research efforts involving both multiscale experiment and multiscale modeling.

It is clear that beyond providing critically needed insight into the physical phenomena operative in complex nanosystems, multiscale modeling tools must be able to predict the structure and properties of novel nanosystems to such a degree that they can guide development of new nanoentities.

The primary challenges facing development of cyber toolkits for computationally guided design of nanosystems (see The Nano Toolbox in Chapter 3) include the following:

- development of theory and associated efficient computational methodologies to accurately reproduce the unique physics and chemistry operative on the nanometer scale, including, but not limited to, those challenges associated with reduced dimensionality, highly correlated systems, and kinetically determined (far from equilibrium) structures
- development of methodologies for bridging length and time scales that accurately capture the influence of the primary physical interactions operative at each scale
- development of analysis tools that calculate the properties (e.g., static and dynamic structure factors) of the modeled nanosystems that can be compared straightforwardly with experiments
- design of cyber toolkits that are sufficiently user friendly and computationally expedient that they can be employed by any competent scientist with minimal training to better understand existing materials, interpret experimental results, or design new materials or devices
- development of expandable model libraries of parameterized multiscale models
- establishment of widely publicized, publicly accessible, well-maintained repositories of freely distributed, validated, and well-documented computational methods, models, and integrated cyber toolkits
- training of scientists and engineers in the use and application of these cybertools

- imaging and visualization capabilities for understanding typical soft matter and interfacial structures
- promotion of interactive feedback between experimentalists and cybertool developers to validate the multiscale models and improve their capabilities and usability

The following paragraphs consider a few examples clearly illustrate the complexity of nanosystmes on multiple scales, the potential role of multiscale modeling, and the need for intimate collaboration between neutron or x-ray characterization and simulation.

Functional Biomimetic Nanodevices. The development of nanoscience is based on its potential relevance for both providing incremental improvements for existing technologies and creating new systems with broad applications to important societal needs such as health, environment, and energy. In the context of new devices, reverse engineering approaches to developing *functional* biomimetic systems is an obvious direction. A potential system might involve self-assembling "nanotracks" (artificial microtubules), molecular motors, and a power source (e.g., ATP) to transport molecules (encapsulated in nanobags or vesicles) and to ultimately carry out nanoscale-directed, nondiffusive synthesis. Most of the building blocks would be replaced with synthetic polymeric and colloid assemblies to determine the minimalist conditions for a self-contained structure that can be externally addressed and controlled. These multicomponent devices often involve a range of hierarchical assemblies that are a mixture of self-organization and directed construction. For example (see Fig. 2.19), the fundamental building blocks of microtubules are two similar proteins, α and β tubulin, which (in a proper aqueous buffer) self-assemble into long protofilaments that, in turn, organize into hollow, 24-nm-diameter microtubules. It is crucial to be able to probe simultaneously the hierarchy of nanoscales when designing and synthesizing the nanotracks using a combination of multiscale modeling and experimental methodologies. Neutrons and x-rays are critical tools to allow for the needed multiscale structural and dynamical characterization needed to understand the nanoscale property–structure relationships in these complex materials. Such understanding can guide development and provide validation of cyber toolkits for computationally guided design of functional biomimetic nanodevices.

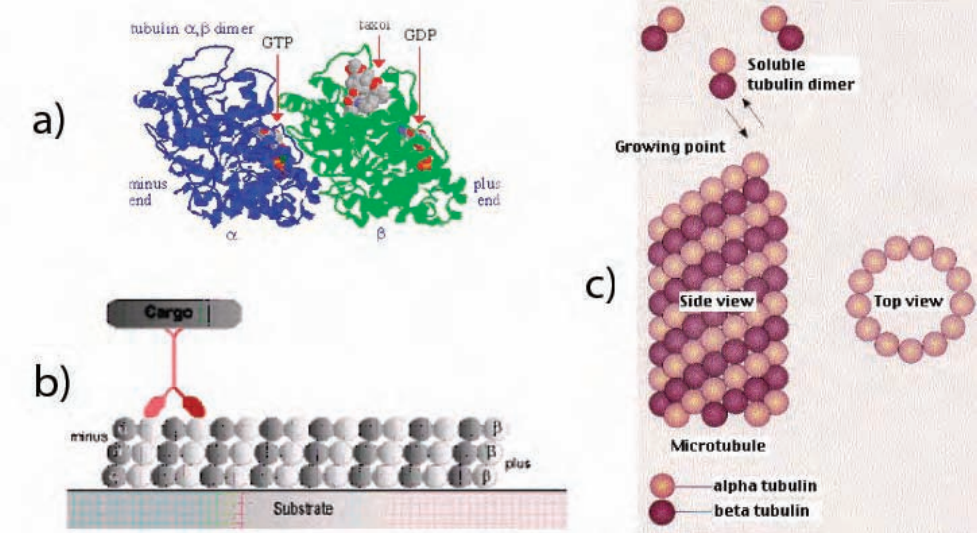


Figure 2.19. Tubulin dimers (a) self-assemble into hollow microtubules (b), which can be used as nanotracks (c) in functional biomimetic systems. (P. Pincus, private communication. (a) Courtesy Joyce Diwan, Rensselaer Polytechnic Institute, www.rpi.edu/dept/bcbp/molbiochem/MBWeb/mb2/part1/microtub.htm. (b) Courtesy John Kimball,http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/C/Cytoskeleton.html. (c) Courtesy Konrad J. Böhm, Leibniz Institute for Age Research - Fritz Lipmann-Institute, Jena, Germany, www.imb-jena.de/www_elmi.)

Self-Assembly of Polymer-Modified Nanoparticles. The ability to control the manner in which polymer chains are chemically attached to nanoparticles, such as semiconductor or metallic nanodots, fullerenes, and carbon nanotubes, engenders endless possibilities for design and fabrication of nanostructured materials for a myriad of materials, energy, environmental, and biomedical applications based on the directed self-association of these materials. Successful development of such materials depends on the characterization and fundamental understanding of the multiscale structure and dynamics of these materials; this will be greatly facilitated by development of multiscale static and dynamic neutron scattering methodologies that can exploit a wide range of momentum and energy transfer in a single instrument or a slate of closely associated instruments that examine the same sample. Concurrently, it will be necessary to develop computationally efficient cybertools for such materials based on experimentally validated multiscale models that will allow for computationally guided optimization of chemical structure and processing to obtain the desired behavior, response, and properties of the materials and devices based on nanoparticle self-association.

Nanosystems Far From Equilibrium. Among the important properties of nanoscale systems compared with atomic and molecular systems is the possibility of forming metastable states that could exhibit desirable physical properties. The constrained equilibrium properties, dynamic response, and temporal evolution of these systems are analogous to issues in glassy and granular materials. These unsolved questions are where nanoscale systems could lead to new insights and, possibly, more complete models. Nanosystems, because of their small number of constituent species, can often assemble subject neither to fully thermodynamic or fully kinetic constraints; this is one reason for the immensely rich palette of nanostructures attained by something as simple as copper metal. Such structures can be modeled by generalized Monte-Carlo or (better) rule-based schemes, but no general theoretical approach has yet been fully developed; such a scheme is strongly needed by the scientific and engineering communities if nanostructures are to be understood. Input from neutrons and x-ray probes will provide critical parameters for the formation and validation of the evolving theory and models of these systems.

Breakdown of Theoretical Paradigms at the Nanoscale. At the nanoscale, the typical theoretical approaches that are useful to describe bulk condensed matter systems can break down. Contributing factors are increased surface to volume, loss of periodicity (and hence inapplicability of the Bloch theorem), and reduced dimensionality (leading to strengthening of correlation effects). These effects often engender enormous departures from bulk behavior for systems that are chemically and even molecularly identical. An example from the literature (see Fig. 2.20) is found for a conjugated polymer system where the low dimensionality and the finiteness of the chains lead to dominant Coulombic effects.

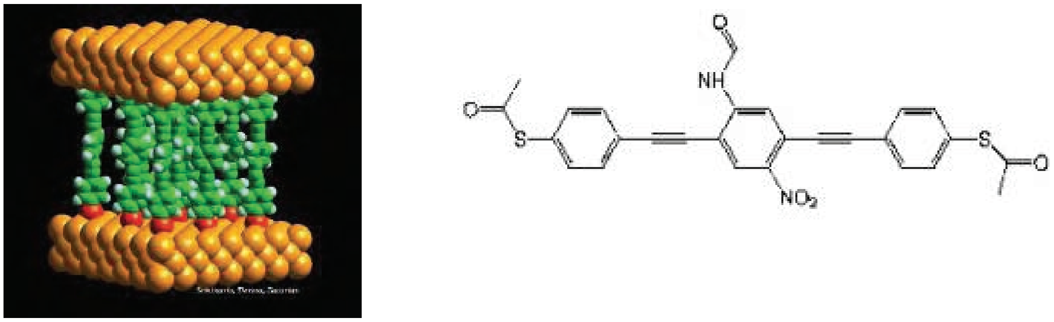


Figure 2.20. Charging effects can be large in small molecules such as the acetate-protected thiol-functionalized molecules shown here, and Coulombic effects cannot be neglected. (Copyright 2003, American Institute of Physics; reprinted with permission from [21].)

Renormalization group concepts for critical phenomena have shown that interaction effects are negligible at high dimensionalities but become dominant below some lower critical dimension, which depends on the particular system under study. Nanosystems often exhibit reduced dimensionality; it is necessary to observe and understand the resulting dramatic departures from bulk behavior. These effects are not restricted to electronic properties. For example, the breakdown of hydrodynamics for fluids in nanopores (as in membranes) is not yet clearly understood. Some of the unanswered questions are: What happens at an ultralow Reynolds number, where biology occurs and where we have nearly no intuition? And what is the role of boundaries on the hydrogen bonding network that is responsible for many of the unusual properties of water? Such issues are exciting challenges for the theoretical community and couple directly to the power of x-ray and neutron probes.

2.6 EARLY CAREER SESSION

Led by Ian S. Anderson, Oak Ridge National Laboratory, and Takeshi Egami, University of Tennessee

Recognizing that researchers at the beginning of their careers will be the most influenced by the directions proposed in the workshop report, the workshop organizers decided that these future leaders in nanoscience and scattering research should be given the opportunity to participate in the meeting and provide their input. Eighteen early-career scientists—graduate students, postdocs, and recently appointed faculty members—were awarded full scholarships to attend the meeting and present their work and ideas. The scholarships were awarded based on the abstracts submitted with the most forward-looking response to one of the following two questions:

- Nanoscience Challenges: What are the most significant future challenges in my research in nanoscience that could be addressed by developments in x-ray scattering and neutron scattering techniques?
- New Scattering Techniques: What significant new capabilities can the developments in scattering techniques that I am working on provide for research at the nanoscale?

The awardees, the majority of which were university based, presented their views to all the workshop participants in a special evening poster session. The posters represented a wide range of scientific disciplines and experimental techniques, and all explicitly recognized the technological needs and goals of their research work. Research goals spanned scientific disciplines from physics to materials to biological and polymer sciences. A large range of complementary experimental techniques such as AFM, light scattering, microwave spectroscopy, TEM, NMR, calorimetry, ellipsometry and magnetometry were displayed across the session, with a very apparent need for more access to neutron and x-ray analysis. The range of scattering techniques being used was also extensive, such as small-angle scattering, reflectometry, and diffraction. Many individual investigators used more than one scattering technique in their work, often including both neutron and x-ray data. Experiments and simulations performed in university-based labs was frequently complemented with scattering work carried out at national facilities, taking advantage of the superior fluxes and diverse techniques available under their general user access programs. In fact, a number of the presentations showed new developments that are possible only at these major facilities, such as resonance reflectivity, fluctuation microscopy, time-resolved microdiffraction, magnetic microscopy, and neutron spin echo.

The scientific disciplines represented covered a wide range of topics, although soft matter clearly dominated. By far the most common theme was polymer science—for templating applications, property modification, polyelectrolytes, or synthetic biological "mimics." Despite the strength of x-ray and neutron scattering techniques for the study of magnetic and dynamic properties of materials, few of the presentations included measurements of this type, even when the participant recognized the need for such data. This situation could point to a lack of general understanding of the full capabilities of the techniques or the perceived complication of data interpretation. The Nano Toolbox (Section 3.4) will help expand the opportunities for newcomers in the scattering fields.

Overall, participants in this session thought that increased source flux for both x-rays and neutrons was essential for advancing their particular research areas. Some stated that specific advances in small-angle scattering should include micro-SANS and, similarly, micro-small-angle diffraction (SAX) to enable hierarchical structures to be studied and to enable fast scanning measurements. All requested the need for more advanced (i.e., subnanosecond), time-resolved diffraction experiments, and measurements of dynamic processes extending from the microsecond regime to the millisecond regime for nanometer-scaled materials.

This session pointed out clearly that the major user facilities play a crucial role in enabling the future of nanoscience research. The paucity of presentations referring to measurement of either dynamic or magnetic properties could point to the need for more training opportunities for underused techniques from among the national user base of expermental methods and software analysis tools.

2.7 REFERENCES

1. D. D. Fong, J. A. Eastman, G. B. Stephenson, P. H. Fuoss, S. K. Streiffer, C. Thompson, O. Auciello. *In situ* synchrotron x-ray studies of ferroelectric thin films, *Journal of Synchrotron Radiations*, 12, 163-167 (2005). doi:10.1107/S0909049504025816
2. H. N. Lee, H .M. Christen, M. F. Chisholm, C. M. Rouleau, D. H. Lowndes, Strong polarization enhancement in asymmetric three-component ferroelectric superlattices, *Nature* **433**, 395–399 (2005). doi:10.1038/nature03261
3. S. Narayanan, J. Wang, X. M. Lin, Dynamical Self-Assembly of Nanocrystal Superlattices during Colloidal Droplet Evaporation by in situ Small Angle X-Ray Scattering, *Physical Review Letters* **93**, 135503 (2004). doi:10.1103/PhysRevLett.93.135503
4. R. A. Segalman, Patterning with block copolymer thin films, *Materials Science and Engineering: R: Reports* **48**, 191 (2005). doi:10.1016/j.mser.2004.12.003
5. R. G. Egres, N. J. Wagner "The rheology and microstructure of acicular precipitated calcium carbonate colloidal suspensions through the shear thickening transition", *Journal of Rheology* **49**(3), 719–746 (2005). doi:10.1122/1.1895800
6. R. Das, T. T. Mills, L. W. Kwok, G. S. Maskel, I. S. Millett, S. Doniach, K. D. Finkelstein, D. Herschlag, L. Pollack, Counterion distribution around DNA probed by solution x-ray scattering," *Phys. Rev. Lett.* **90**(18), 188103 (2003). doi:10.1103/10.1103/PhysRevLett.90.188103
7. H. Ohldag, T. J. Regan, J. Stöhr, A. Scholl, F. Nolting, J. Lüning, C. Stamm, S. Anders, R. L. White, Spectroscopic identification and direct imaging of interfacial magnetic spins, *Phys. Rev. Lett.* **87**(24), 247201 (2001). doi:10.1103/PhysRevLett.87.247201
8. M. Arenz, U. Landman, U. Heiz, CO combustion on supported gold cluster, ChemPhysChem, 7(9) 1871–1879 (2006). doi:10.1002/cphc.200600029
9. B. Yoon, H. Häkkinen, U. Landman, A. S. Wörz, J-M. Antonietti, S. Abbet, K. Judai, U. Heiz, Charging effects on bonding and catalyzed oxidation of CO on Au_8 clusters on MgO," *Science* **307**(5708), 403–407 (2005). doi:10.1126/science.1104168

10. J. A. Rodriguez, J. C. Hanson, A. I. Frenkel, J. Y. Kim, M. Pérez, Experimental and theoretical studies on the reaction of H_2 with NiO: Role of O vacancies and mechanism for oxide reduction, *J. Am. Chem. Soc.* **124**(2), 346-354 (2002). doi:10.1021/ja0121080
11. R. L. Cropley, F. J. Williams, A. J. Urquhart, O. P. H. Vaughan, M. S. Tikhov, R. M. Lambert, Efficient epoxidation of a terminal alkene containing allylic hydrogen atoms: *trans*-methylstyrene on Cu, *J. Am. Chem. Soc.* **127**, 6069-6076 (2005). doi:10.1021/ja042758e
12. M. S. Dresselhaus, I. L. Thomas, Alternative energy technologies, *Nature* **414**, 332–337 (2001). doi:10.1038/35104599
13. E. Mamontov, T. Egami, Structural defects in a nano-scale powder of CeO_2 studied by pulsed neutron diffraction, *J. Physics and Chemistry of Solids* **61**(8), 1345-1356 (2000). doi:10.1016/S0022-3697(00)00003-2
14. T. Arnold, S. Chanaa, S. M. Clarke, R. E. Cook, J. Z. Larese, Structure of an *n*-butane monolayer adsorbed on magnesium oxide (100), *Phys. Rev.* B **74**, 085421 (2006). doi:10.1103/PhysRevB.74.085421
15. J. B. Kortright, O. Hellwig, K. Chesnel, S. Sun, E.E. Fullerton, Interparticle magnetic correlations in dense Co nanoparticle assemblies, *Phys. Rev. B* **71**, 012402 (2005). doi:10.1103/PhysRevB.71.012402
16. C. A. Larabell, M. A. Le Gros. X-ray tomography generates 3-D reconstructions of the yeast, *Saccharomyces cerevisiae*, at 60-nm resolution, *Mol. Biol. Cell* **15**, 957 (2004) doi:10.1091/mbc.E03-07-0522
17. I. K. Robinson, I. A. Vartanyants, G. J. Williams, M. A. Pfeifer, J.A. Pitney, Reconstruction of the shapes of gold nanocrystals using coherent x-ray diffraction, *Phys. Rev. Lett.* **87**, 195505 (2001). doi:10.1103/PhysRevLett.87.195505
18. G. J. Williams, M. A. Pfeifer, I. A. Vartanyants, I. K. Robinson, Three-dimensional imaging of microstructure in Au nanocrystals, *Phys. Rev. Lett.* **90**(17), 175501 (2003). doi:10.1103/PhysRevLett.90.175501
19. P. Fenter, C. Park, Z. Zhang, S. Wang, Observation of subnanometre-high surface topography with x-ray reflection phase-contrast microscopy, *Nature Phys.* **2**, 700-704 (2006). doi:10.1038/nphys419
20. S. Narayanan, D. R. Lee, R. S. Guico, S. K. Sinha, J. Wang, Real-time evolution of the distribution of nanoparticles in an ultrathin-polymer-film-based waveguide, *Phys. Rev. Lett.* **94**, 145504 (2005). doi:10.1103/PhysRevLett.94.145504
21. J. Reichert, H. B. Weber, M. Mayor, H. Lohneysen, Low-temperature conductance measurements on single molecules, *Applied Physics Letters* **82**, 4137 (2003). doi:10.1063/1.1574844

3. Research Target Areas

This chapter presents seven cross-cutting research areas that were identified by the workshop chairs and leaders of the breakout sessions. For each area, they have drawn on the discussions and recommendations of several breakout groups to envision new or expanded roles for scattering researchers within nanoscale science and engineering. Targeted research programs in these areas would accelerate and broaden the impact of x-ray and neutron science upon the nanotechnology community.

3.1 DYNAMICS: LESSONS FOR NANOTECHNOLOGY FROM NATURE

As nanoscience develops to the point where it can mimic nature more and more, and as the science matures into nanotechnology, it has the potential to profoundly reshape the world around us. Using new scattering techniques to directly measure dynamic processes on time scales of attoseconds—compared to the millisecond resolution available today—will provide crucial information on the dynamic processes that drive replication, assembly, folding, and functioning in complex biomimetic systems at the nanoscale. This information will provide insights into dynamic processes across a range of disciplines: for example, the processes that govern the function of membranes, allowing them to regulate the passage of information and materials in and out of living cells.

Dynamic processes in nature cover an enormous range of time scales (see Fig. 3.1), from fast electron transfers in bonding processes or photosynthesis, through molecular vibrations to folding motions, to the "breathing" of proteins and wrapping of nucleosomes.

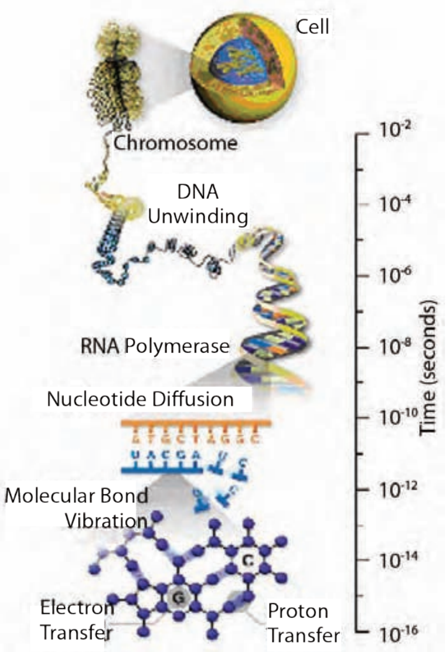


Figure 3.1. Biological structures and functional systems versus time. Note that the proton transfer occurs at 10^{-17} s where x-rays measure electron/protron transfer; molecular vibrations occur at 10^{-12} s, where neutrons measure thermal strains. Applying this knowledge to artificial structures opens new horizons for nanomaterials. (Courtesy of Oak Ridge National Laboratory.)

These motions are essential for biological function. Through evolutionary design, nature has learned how to make use of this vast time range so that the very essence of the assembly and functional processes that take place on relatively slow time scales are actually predetermined by much faster processes at the electronic level.

Furthermore, nature takes advantage of unique phenomena at the nanoscale through the correlated electronic and structural dynamics imposed by specific nanoscale architectures. In photosynthesis, for instance, a cascade of dynamic events evolves throughout the duration of energy-converting processes that follow photon absorption and subsequent charge transfer events. The fate of the photon following absorption, varies depending on the nature of the nanoscale cofactor environment presented by each of the protein photosynthetic protein sites. Induced electronic structure distortions, and subsequent distortions of the ions following charge separation, are thought to play an essential role in the protein's ability to separate and store charge efficiently. Such charge-induced distortions are common to a broad range of important nanoscience problems, including molecular electronics, photovoltaics, and catalysis. For example, the fate of an ion plays a critical role in an electronic device's ability to store information.

Although there has been progress in the development of novel biomimetic materials, these are essentially improvements to static structures and function. In the future, smart designs that imitate nature's approach to dynamically controlled processes will lead to a myriad of new applications, including biosensors, microfluidic devices, and smart scaffolds for tissue engineering, and the use of cells to build thousands of functional nanomachines. Understanding the complex relations between nanoscale structure and function in biological materials will provide invaluable insights into the "tricks of the trade" that will enable these technologies—and x-rays and neutrons are among the best tools for these investigations.

X-ray and neutron techniques are unique in their ability to probe the complete range of time scales of interest in nature and nanoscience, via time-resolved scattering and spectroscopic techniques, at the relevant length scales. Furthermore, the techniques are truly complementary. Current x-ray probes are capable of determining the electronic and structural dynamics of individual nanostructures (see Fig. 3.2), while neutrons measure the dynamic response of assemblies of nanostructures—with the additional capability of separating a single particle from collective dynamics.

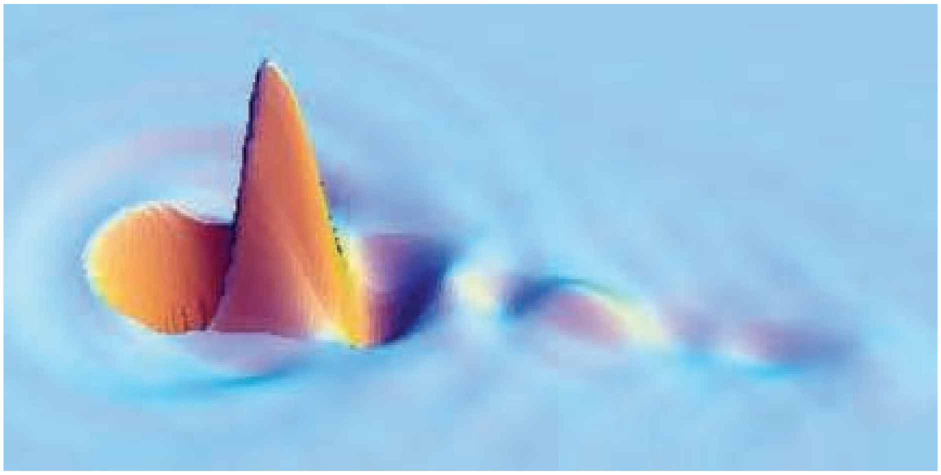


Figure 3.2. Attosecond snapshots of electronic disturbances in water calculated to be produced by a diffusing gold ion based on inelastic x-ray scattering measurements. (Copyright 2004 by the American Physical Society; reprinted with permission from [1].)

For example, modern x-ray facilities allow study of atom-specific electron transfer mechanisms to determine the temporal evolution of the electron wave packet on femtosecond time scales. On the same time scale, deep inelastic neutron scattering can probe the nuclear wave functions, giving a direct measurement of single-particle nuclear motions, which samples the local environment and enables reconstruction of effective Born-Oppenheimer potentials. A grand challenge lies in measuring the ground- and excited-state structural landscapes and electronic structures of the bonding states for complex molecular systems. The excited-state energies are on scale of bonding energies (i.e., electron volts, corresponding to subfemtosecond time scales), while the subsequent ionic distortions occur and propagate on picosecond time scales and could promote structural changes on the millisecond scale.

3.2 NANOMATERIALS: UNDERSTANDING THE IMPACT OF THE REAL WORLD

It is a major challenge to understand, manipulate, and control the structure and dynamics of a nanomaterial while varying environmental factors such as temperature, pressure, electric or magnetic fields, stress or shear, or pH. Gaining this ability would have great consequences for real-world applications of nanotechnology and for commercialization of nanoscale processes. The response of a nanomaterial to its environment can drastically alter the nanomaterial's properties, function, and performance.

Taking advantage of unique properties of material which emerge at 1 to 100 nm length scales is the fundamental strategy of nanotechnology. The huge surface area-to-volume ratio of nanomaterials—i.e., the large fraction of the atoms which are at a surface—can amplify environmental effects; a nanomaterial's form and function can change drastically in response to minor real-world changes. Understanding how to preserve and even manufacture or control these forms and functions is one of the major hurdles facing the research community as nanoscale materials become technological and commercial realities.

A ubiquitous process in our daily lives—catalysis—is one case where understanding the impact of the real-world environments at the nanoscale is critical. In applications ranging from catalytic converters in vehicles to a variety of industrial processes, catalytic nanomaterials are one of the best examples of the challenging areas in nanoscience. For instance, a catalytic converter (Fig. 3.3) consists of dispersed nanoparticles of platinum (Pt), rhodium (Rh), cesium (Ce), zirconium (Zr), and lanthanum (La) impregnated in an alumina washcoat material. The thin alumina washcoat covers the honeycomb walls in the catalytic converter.

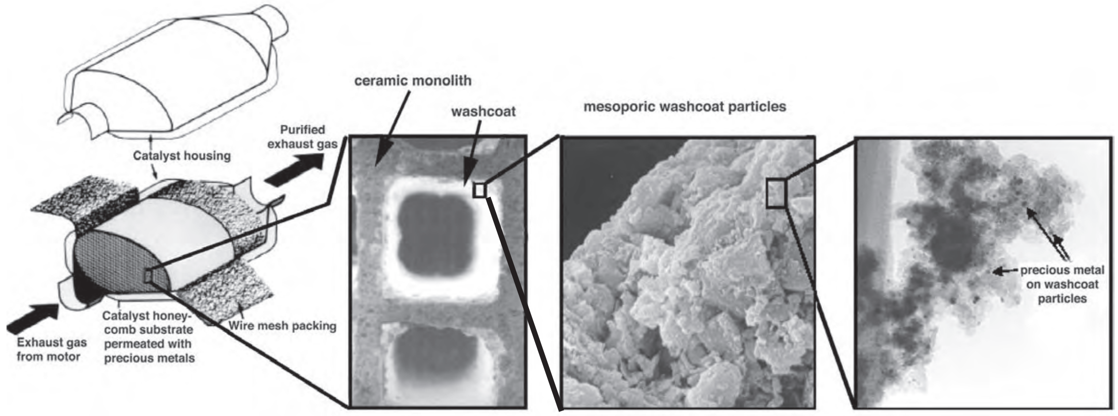


Figure 3.3. Illustration of the placement of nanoparticles in automotive catalytic converters. (Copyright 2003 AAAS; reprinted with permission from [2].)

The local size and composition of the catalyst nanoparticles greatly affect their performance (activity and selectivity). Therefore, the importance of characterizing the nanoparticles in real environments has stimulated extensive efforts to develop *in situ* tools.

Neutron and x-ray techniques are already contributing to characterization, and sometimes control, of the behavior of catalysts and other nanomaterials in unique environments. Structural studies using elastic and inelastic neutron scattering methods are used to characterize bulk nanoscale catalysts and the adsorbed molecular species that participate in various chemical processes upon or within them. Typical studies include determination of local disorder, particle-size distributions, and structures of molecules containing low-atomic-number atoms adsorbed or entrained within the nanocatalysts.

As a complement, high-resolution x-ray scattering studies are providing data at nanometer-length scales and high temporal resolution. This technique has the ability to spectroscopically probe the bonding and chemical composition at the surface and at buried interfaces for a broad range of environmental conditions.

Another example is the mechanical properties of polymers under pressure. At atmospheric pressure the mechanical response of typical polymer binders in polymer-nanoparticle composites is rubbery. However, the actual pressures present during mechanical loading of these materials can be extreme, on the order of kbars. At such high pressures, the entire polymer relaxation time spectrum is increased dramatically, producing local hot spots with temperature rises of order 1000°C. Furthermore, the shift of the effective glass transition temperature due to high pressures can couple strongly with the nanoscale confinement effects. This coupling between pressure and nanoscale confinement is essentially unexplored, due largely to the lack of experimental probes of polymer dynamics that can operate under high pressure with the appropriate spatial and temporal resolution. The future application of dynamic neutron scattering to polymer–particle composites under high pressure will provide revolutionary advances in understanding the influence of pressure and nanoscale confinement on the dynamics of polymer matrices in polymer particle composite materials critical to the design and processing of novel viscoelastic nanocomposites.

Far-reaching ideas for the future focus on using time-spin-based modulation techniques and small-angle neutron scattering to allow researchers to obtain three-dimensional reconstructions from quasi-elastic scattering spectra. Some predict that combining a pulsed source's time modulation with a two-dimensional detector will allow holographic imaging on 10 to 500 nm length scales of, for example, a nanoclustered material as it goes through a chemical transition.

3.3 EXTREME ENVIRONMENTS

The ability to understand or control the structure and dynamics of nanoscale materials under extreme conditions, such as high and low temperatures, megabar pressures, and mature stresses and strains, is at the forefront of major scientific and technical challenges facing our future. One of the major scientific findings to have emerged from last century is the profound effect of extreme conditions on the nature of materials. The remarkable changes introduced in materials by subjecting them to high pressure or high magnetic fields combined with variable temperatures from the millikelvin range to thousands of degrees is essential for understanding problems that span the physical and biological sciences. New technical developments and new materials and engineering approaches have opened windows for considering such extreme sample environments for x-ray and neutron studies of nanomaterials.

At high pressures, now available in the laboratory to millions of atmospheres (several hundred gigapascal), gases can become superconductors; novel electronic, magnetic, and superhard materials can be formed; unreactive noble elements can be made reactive; and new chemical and biochemical pathways can be switched on. At high magnetic fields, novel phases of condensed matter can be explored. Quantum phase transitions and new robust phases of superconductivity (as well as new paths to materials processing) could lead to breakthroughs in novel materials with enhanced performance, including bulk nanocrystalline phases and advanced nanomagnetic materials. These extreme environments thus introduce a unique and essential variable for the discovery of entirely new and technologically important materials. Examples include new methods of synthetic high-pressure chemistry to incorporate elements into clathrate and zeolite structures for creation of new catalysts, as well as into storage materials for gases such as hydrogen (Fig. 3.4).

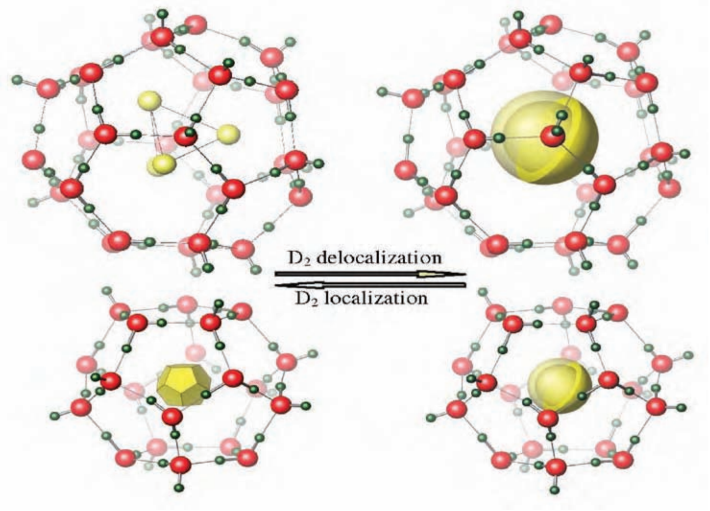


Figure 3.4. Hydrogen-rich clathrate hydrate compound containing up to 5 wt% hydrogen formed at 0.5 GPa are stable under ambient pressure to temperatures as high as 145 °K. Neutron scattering experiments reveal an order–disorder transition in the $(H_2)_4$ cluster on cooling below 100 °K. (Copyright 2004 by the American Physical Society; reprinted with permission from [3].)

For almost 50 years the diamond-anvil cell has been instrumental in studies of bulk materials at static pressures from ambient to > 300 GPa (Fig. 3.5) and at very high temperatures (> 7000 °K) and low temperatures (14 mK). Although the basic device is well established, major breakthroughs in the technology are completely changing the status quo. For instance, studies have been limited to small access angles in forward-scattering geometry, but with the invention of panoramic cells, nearly complete spherical coverage of reciprocal and momentum space has become accessible. With improvements in x-ray- and neutron-transparent gaskets, wide wavelength (or energy) ranges have opened up for elastic and inelastic scattering. Focusing x-rays to < 100 nm and neutrons to < 50 µm allows us to investigate the elasticity and rheology of single grains at extraordinary pressures with unprecedented detail. Moreover, these focusing techniques continue to improve, and an order of magnitude higher focusing is likely within the next few years. Meanwhile, the development of giant synthetic single-crystal diamonds holds the promise of subjecting millimeter-size samples to multimegabar pressures, while at temperatures from millikelvins to kilokelvins.

Such technological advances will have profound impacts on questions that surround the inorganic-organic interface—geobiology—an area central to major environmental issues as well as to fundamental questions about the limits of life in extreme environments and the origin of life itself. This is an area where nanoscience has only scratched the surface.

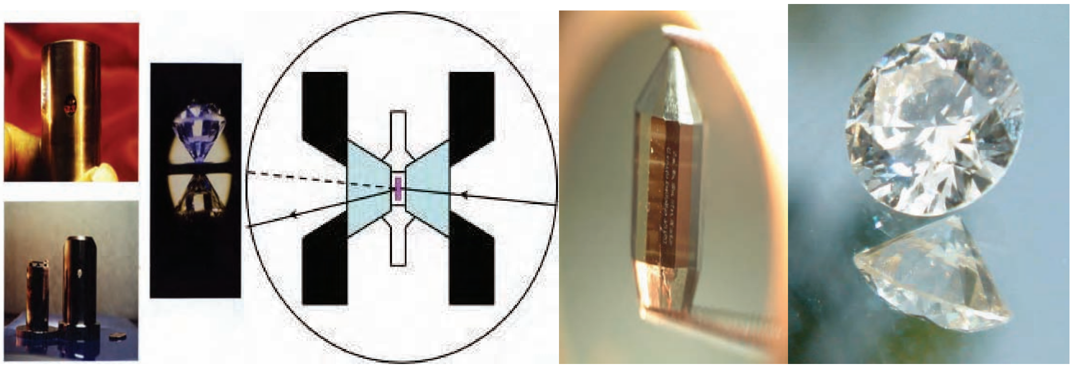


Figure 3.5. Diamond anvil cells (left image) make it possible for researchers to probe materials at pressures up to multimegabars (> 300 GPa) with x-rays. The center left image is a schematic of a diamond-anvil high-pressure cell. New synthetic large single-crystal diamonds will also allow neutron scattering measurements under such extreme pressures. Diamonds cut from 10 and 1 carat blocks of single crystal synthetic diamond are shown in the center right and far right images. (Courtesy of R. J. Hemley and H. K. Mao [4]).

Determination of the limits of life in extreme environments requires direct *in situ* study of the viability of living cells (including cell membrane integrity), constraint of biochemical activity at the molecular level, monitoring cell growth and division, and detailed examination of pressure-temperature-composition effects on related chemical reactions. To answer specific questions regarding survival mechanisms of microorganisms under high-stress (extreme) environments, it is essential to monitor ongoing biochemical and microbiological processes with the types of *in situ* imaging techniques now being applied under ambient conditions. These studies include detailed examination of single cells and their components' ultrastructure, membranes, and macromolecules under stress. Such study would allow detailed examination of adaptation and mutation—evolution—at the molecular level in a test tube, work that would open new fields such as high-pressure genomics and proteomics. The initial groundwork for this new generation of experiments has already been laid with emerging technology.

An emerging generation of synchrotron and neutron facilities, coupled with more sophisticated pressure-temperature devices, would enable an exploration of nanomaterials in a much broader range of conditions, specifically allowing imaging in entirely new domains of length scales, as well as pressure and temperature. With new classes of smart, large-volume devices, such as those made possible by new diamond technologies, entirely new measurements of material properties could be performed. These imaging studies would combine simultaneous diffraction, spectroscopy, and transport measurements. The goal is to perform measurements with accuracy, precision, and sensitivity that exceed those currently allowed in studies under ambient conditions. Thus the full suite of techniques now used for exquisite studies of nanoscale problems in chemistry, physics, and biology can be conducted under the most extreme conditions, where physical, chemical, and biological properties can be precisely tuned to produce new phenomena.

New technical developments point to a new paradigm in considering sample environments for x-ray and neutron studies of nanomaterials. Our goal is to have large-volume samples (> 1 mm^3 samples) at 300 GPa, while at the same time allowing the broadest possible temperatures. This requires a new generation of devices with windows and anvils in the > 100 carat range. With these developments, we could move from single-phase diffraction/scattering measurements to tomographic imaging of materials under extreme conditions using the new generation of nanometer x-ray beams and micron-scale neutron beams. The time structure of synchrotron x-ray and neutron sources will be exploited to examine for the first time chemical dynamics under extreme conditions. Ultimately, these experiments must take advantage of coherent sources and will allow a broad range of questions from detonation to biochemical reactions in living cells to be addressed directly. Additional experiments would involve a combination of static and dynamic compression techniques to allow access to entirely new pressure–temperature domains, such as those found within newly discovered extrasolar planets and even stars. Finally, these high-pressure/variable temperature x-ray and neutron methods can be integrated with techniques such as intense magnetic fields and laser methods to address altogether new questions at the nanoscale that will surely emerge in the future.

3.4 USER-FRIENDLY MODELING: THE NANO TOOLBOX

In their diversity and richness, nanostructures pose problems concerning structure/function relationships that are more varied and challenging than those arising in homogeneous materials. Achieving the goal of completely characterizing a nanostructure, and using this knowledge to design new structures, requires the combination of multiple experimental techniques, together with fundamental theory and the modeling and simulation capabilities offered by modern computing infrastructures.

For example, determination of the structure of ensembles of nanoparticles that lack periodic long-range order is an extremely challenging problem because of the scarcity of information in the available data. No currently available scattering or imaging method yields direct *ab initio* nanoparticle structure solutions with subangstrom resolution. One approach developed at Michigan State University is to obtain high-resolution structures by combining total scattering methods (such as the atomic PDF approach, which yields weighted distributions of inter-atomic distances), other structural and imaging techniques (such as EXAFS, electron microscopy, and NMR spectroscopy), and advanced computer modeling.

Figure 3.6 shows a recent breakthrough reconstruction of the buckyball C_{60} structure, *ab initio*, from PDF data alone using a novel promotion-relegation algorithm.

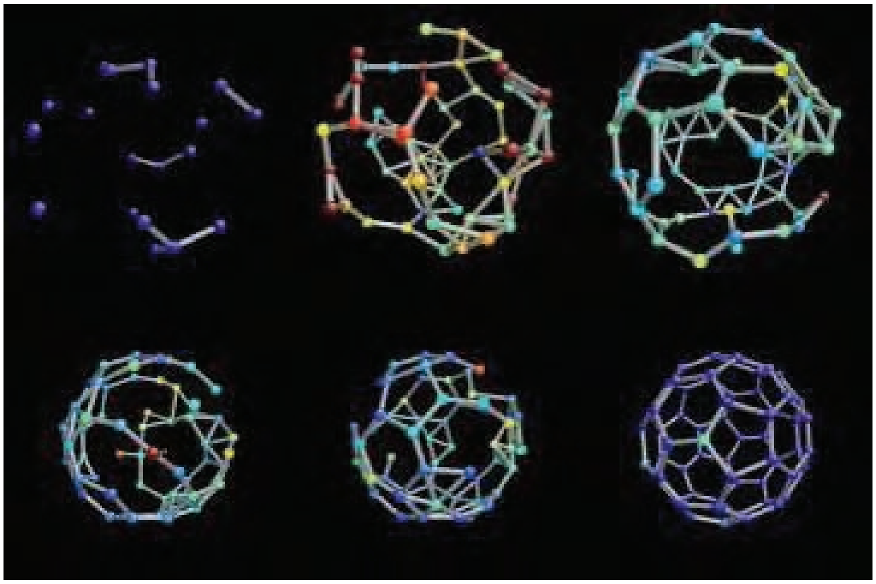


Figure 3.6. Intermediate and final clusters in the *ab initio* search to find the structure of C60 from neutron pair distribution function data. Atoms are added and removed from the cluster at each step, depending on their agreement with the geometric distances obtained from the pair distribution function data. (Reprinted from [5] by permission from MacMillan Publishers Ltd.)

The tremendous growth of modeling, becoming a third branch of scientific inquiry along with experiment and theory, offers an avenue to harness structural, dynamical, and response properties observation to provide deep insights into nanoscale structure/property schemes—to enable nanomaterials by design. To turn these promises into reality, the community must, over the next decade, provide individual researchers with access to rich resources such as standardized databases, advanced instrumentation facilities, and grid computing. To do this realistically will require modeling tools with a new level of user-friendliness, which we call the Nano Toolbox.

An exciting opportunity lies in development of the Nano Toolbox. As envisioned, this resource would be an integrated modeling toolbox of programs, graphics, data, scripts, and interfaces individually tailored to, and developed by, individual researchers. Each researcher could craft their own toolkit and have it available to them with full reliability wherever and whenever they choose. The Nano Toolbox could reside on several nodes of the universal computing grid, as well as on local resources ranging from a personal computer to an industry, lab, or commercial computing center. This grid-based modality means instant portability and a new level of capability.

The Nano Toolbox concept, coupled with standardization of databases, is key to solving vexing problems that have slowed or gridlocked traditional modeling applications. For example, a newly prepared bimetallic nanopyramid particle could be analyzed by combining EXAFS, SANS, and radial distribution function methods, as well as optical, vibrational, and nuclear magnetic resonance spectroscopies, scanning probe microscopy and transmission electron microscopy. These data would be analyzed and modeled by the Nano Toolbox, and putative structural and response properties computed. Database comparison with known structures and properties would be crucial in defining the modeling. Computational tools, including electronic structure and molecular dynamics calculations, would then be employed to compute appropriate response and structural behaviors to test the consistency of the structure–function scheme.

The computational power offered by modern grid-based computing is essential if data is to be extrapolated down to atomic-scale precision. This visionary initiative will be transformative for the application of advanced x-ray and neutron techniques to nanoscience. The so-called “imaging paradigm” that plagues traditional interpretation of reciprocal space data could be broken, allowing nonspecialist users of advanced scattering techniques to “see” the results of their measurements in a form that they can understand and to have access to the relevant information, or final product. In the future, this capability must be provided in real time (i.e., during the experimental process) so that experimenters can intelligently steer their measurements and experimental protocols to maximize the information content in their results. Extrapolating to the longer term, the visions enabled by the Nano Toolbox will permit researchers to interact collectively in real time at all stages of characterization, modeling, and simulation, whether collecting data at a facility or working from their home institutions. Extending this capability to the classroom, the Nano Toolbox will enable the full development of human resources in the scientific community and provide the human capital for the science of the next generation.

3.5 NANOPARTICLES: THE ULTIMATE IN PRECISION METRICS

Future generations of nanotechnologies, from quantum computation to light harvesting for energy, will be based on new nanoscale materials and devices that operate with only a few electrons. In many cases one—and only one—atom must be introduced into a host nanoparticle to realize the intended application, for example as qubits for quantum computing. Potential synthesis routes are being developed to achieve single-atom control, but they cannot be successful in the absence of the capability to detect and visualize a single atom buried inside an object.

Although not possible today, in the next 10 years x-ray nanoprobes at third- and fourth-generation synchrotron sources will enable the nondestructive detection of a single atom embedded in a nanosized object. Using spectroscopy and scattering techniques combined with advanced focusing optics and photon and electron-yield detectors, it will be possible to identify an individual atom and determine its chemical bonding state, its position, and the structure of the surrounding atoms. Such measurements will complement other techniques (such as scanning probe microscopies) that probe individual atoms near surfaces.

Combining theoretical models with today's state-of-the-art computational tools, it is possible to perform a "computational experiment" to predict the effects of a single atom on the thermal, electronic, and mechanical properties of a host nanoparticle. Figure 3.7 shows a recent "density functional" calculation that predicts how the position of a nitrogen atom, whether located near the core or at the surface, determines whether or not the atom can "donate" one of its electrons to the diamond nanocrystalline particle. More generally, the goal of single-atom detection is a Holy Grail for many fields, for example, in understanding modification of mechanical properties of grain boundaries by impurities. This method provides information both on the interior of the object and on defects within the object. Progress in lensless imaging, including achievement of higher spatial resolution, depends critically on the availability of ultra-coherent x-rays such as those from the so-called fourth-generation x-ray synchrotron sources currently under development in the United States and worldwide.

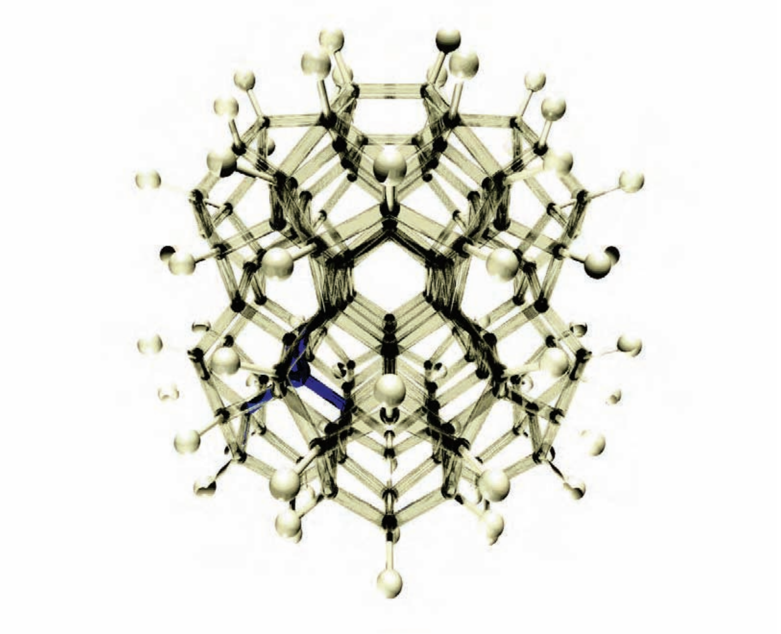


Figure 3.7. Advanced theory and computation provide us with a tool to predict the effect of a single atom on a host nanoparticle. This image shows the calculated structure of a diamond nanocrystal with a nitrogen atom substituted on a single carbon lattice site. In the near future it will be possible to experimentally measure a single dopant atom embedded in a nanoparticle. (Courtesy A. Barnard.)

Nanometer-scale x-ray beams from specially designed third- or fourth-generation synchrotron nanoprobe beam lines are the key to rapid single-atom detection and nondestructive quantification. The primary challenge for nanoprobe beam lines is fabrication of x-ray optics that produce diffraction-limited beams. Fresnel zone plates, like the one shown in Fig. 3.8, are one approach to diffraction-limited optics; others include x-ray mirrors and multilayer Laue lenses that could within the next 10 to 20 years produce 1 nm hard x-ray beams. Once achieved, the raw count rates would be sufficient for detecting signal, such as fluorescence, from a single atom. Imaging will be possible when detection of fluorescent x-rays is combined with advanced tomographic techniques.

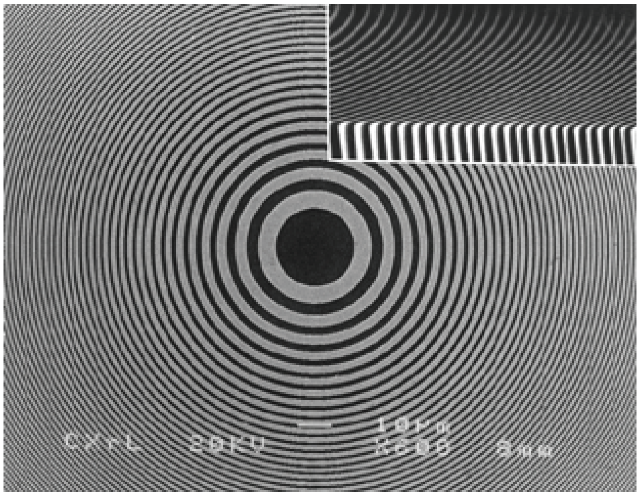


Figure 3.8. X-ray zone plates, like the one shown here, are one possible approach to diffraction-limited, sub-nanometer beams. Zone plate fabrication for 1 nm x-ray beams goes well beyond today's state-of-the-art fabrication techniques. (Courtesy Wenbing Yun, Xradia, Inc.)

Although it is unlikely that neutron-based techniques will ever achieve the sensitivity required to study a single nanoparticle, they do provide the complementary information often necessary for complete characterization, obtained from the average properties of an ensemble of particles. In particular, neutron techniques are essential for the detection of light elements. A good example is the determination of the structure of disordered ceria nanoparticles used as oxygen reservoirs in catalytic converters. Neutrons also provide essential information on dynamical properties, which cannot be obtained by any other technique. The range of applications will be extended by the emergence of new neutron-focusing methods, which will extend neutron measurements to much smaller sample volumes than would have been possible previously. Neutron beams can be focused in space using reflection from mirrors (nondispersive) or refraction through material or magnetic lenses (dispersive). For example, neutron focusing with Kirkpatrick-Baez supermirrors enables flux gains of more than 100 for neutron beams less than $200 \times 200\ \mu\text{m}^2$. Currently, beam dimensions of $< 100\ \mu\text{m}$ are achievable. In the future, nested arrangements of KB mirrors will allow collection of a wider range of source divergence, leading to even more intense micron-sized beams. This improved flux density for small beams will be essential to achieve adequate signal and the best signal-to-noise for small sample volumes, and will enable the range of *in situ* measurements to be extended to higher limits of temperature, pressure, and magnetic field. Looking further into the future, coherent transmission through nanometer-sized neutron waveguides will open up the possibilities to perform microdiffraction, obtain speckle patterns, and acquire phase-contrast images from nanometer-sized samples. Furthermore, neutron holography promises to provide direct measurement of local crystal lattice and magnetic structure distortion.

3.6 NEXT-GENERATION ELECTRONICS: FOLLOWING A SINGLE SPIN

Magnetism is one of the oldest scientific disciplines, but it is also at the forefront of the emerging nanotechnology era, from application of giant magneto-resistance in today's read heads for hard drives—which incorporate sub-100-nm magnetic elements—to the future vision for spintronics, in which spin rather than charge carries and stores information. Creating future spintronic devices, which will require fabricating structures for injection and manipulation of as little as one electronic spin, hinges on our ability to understand spin distributions and spin currents at short length and time scales in a realistic device—a capability that is not available anywhere in the world today.

Current spintronic devices comprise many layers of nanometer-scale magnetic films whose function depends on selective control of the transmission of electron spin polarization across buried interfaces. Polarized neutron reflectivity of layered heterostructures quantitatively determines both the magnetic and structural depth profile with 0.1 nm resolution and is capable of determining vector orientation of the local magnetic moments with high precision. Recently developed neutron spin manipulation techniques will enable spin orientation to be determined at surfaces with lateral dimensions ranging from nanometers to microns.

New soft x-ray resonant magneto-optical techniques, when combined with advance focusing techniques and the temporal resolution afforded by third-generation synchrotron sources, provide the capability to measure the activity of a small number of electronic spins. By virtue of the polarization of synchrotron x-rays, resonant x-ray techniques provide sensitivity to magnetism as well as element and chemical specificity. Figure 3.9 shows a scanning transmission x-ray microscope image of the magnetic structure of a giant magneto-resistance device where the active region contains thousands of spins. As was recently shown, switching dynamics of such small devices are determined by magnetic vortices that form spontaneously in nanoscale magnetic materials. One of the great advantages to using x-ray techniques is the ability to measure the magnetic response during operation of a realistic device, as can be clearly seen in the figure.

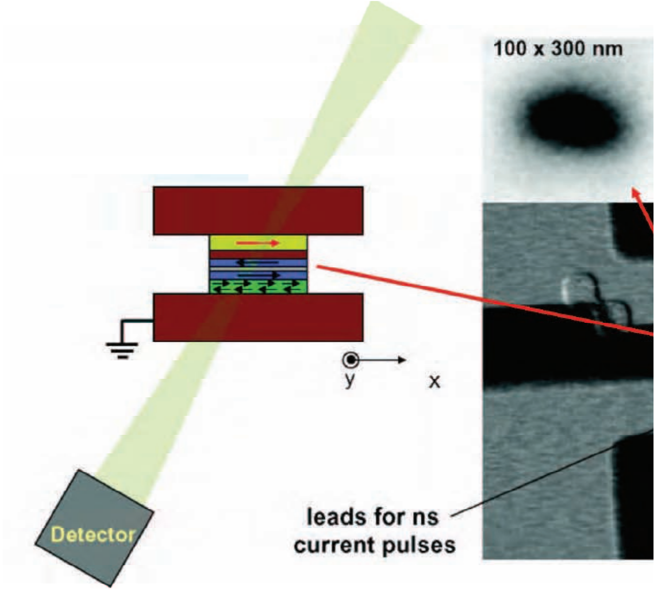


Figure 3.9. Scanning transmission x-ray microscopy reveals the structure and local magnetic properties of a 100 × 300 nm GMR device under a gold capping layer. (Courtesy Joachim Stöhr, Stanford Linear Accelerator Center.)

Complementing x-ray data on the larger scale, neutron scattering will provide a bird's-eye view of the dynamic response of arrays of electron and nuclear spins ranging from metallic nanoparticles, to magnetic vortices, and to single spin quantum dots. Understanding the magnetic interactions that determine function on the nanoscale requires the elucidation of a wide range of dynamics, including intraparticle and interlayer spin waves, single particle reorientations and precessions, domain switching, and collective (inter-particle, inter-layer, and inter-stripe) excitations.

Achieving the goal of measuring a small number of spins, approaching a single spin, will require the development of diffraction-limited optics and ultrafast x-ray techniques. For soft x-rays, the 1 to 2 nm wavelengths set the achievable, diffraction-limited lateral spatial resolution, while for hard x-rays, another factor of ten could be obtainable. Future generations of synchrotron sources, such as the Linac Coherent Light Source (LCLS) Free Electron Laser source at the Stanford Linear Accelerator Center, will provide the necessary flux for diffraction-limited focusing with femtosecond time scales, enabling dynamical studies of spin currents and magnetic switching. Ultimately, the goal is to transcend binary logic and move towards quantum computing strategies that can be implemented via electronic or nuclear spin manipulation using quantum entanglement.

3.7 NANOPROCESSING AND NANOMANUFACTURING

X-rays and neutrons offer a potentially important long-term path for direct fabrication of novel nanostructures. *In situ* diagnostic tools utilizing x-rays or neutrons will help establish stable processes for nanomanufacturing. It is envisioned that x-ray nanobeams will provide revolutionary tools for direct fabrication of novel nanoscale structures in the future. For example, a focused x-ray might be used to write two- and three-dimensional structures by nonlinear photochemical interactions. Today, proximity and projection x-ray lithography provide a means to fabricate in parallel at the nanoscale achievable by serial-write techniques like electron-beam lithography. Because x-rays penetrate deep into a sample, patterns can be written at buried interfaces or line structures with high aspect ratios that can be fabricated deep into the sample matrix. Multiphoton processes could be used to fabricate 3-D structures that can include concentric features and deeply imbedded structures that would be impossible to manufacture by alternative methods.

The range of processes that can be stimulated in a material by neutron or x-ray waves includes phonons, spin waves, electronic transitions, atomic transitions, and local heating. Furthermore, the coherence of the waves can be used to create standing waves, holograms, traveling waves in layers, and precise positioning of the nodes and hence interaction of the wave functions in a material. The precision of these phenomena can be tailored from nanometer to subnanometer resolution. Although atomic positioning has been demonstrated using surface probes such as atomic force microscopy, x-rays and neutrons offer the unique possibility to generate correlated potentials across a relatively large surface area governed by the tunable coherence length of the radiation. Furthermore, because they penetrate below the surface, x-rays and neutrons have the potential to enable 3-D assembly at subnanometer resolution.

Although similar neutron applications tend to suffer from the low intensity beams, high-efficiency capture processes can be used to mark the nodes from a coherent wave pattern. Today, the promise of manufacturing of nanostructures with neutron probes is as yet untapped. However, the growing use of x-rays—which were unused in manufacturing just a few decades ago—suggests that the potential also exists for neutrons to develop into tools for fabrication of nanosystems.

High-yield processing of functional nanomaterials and manufacturing of nanoscale devices is critical to realizing the economic benefits of nanotechnology. As an example, the semiconductor manufacturing industry, a $228B-per-year world market in which U.S. companies hold leading positions, now produces chips in high volume with gate widths of < 50 nm and clock speeds near 3 GHz. These are currently produced using optical lithography in the deep ultraviolet, with radiation wavelengths in the 193 to 248 nm region. Beginning in 2009 to 2010, manufacturing is expected to shift to the use of extreme ultraviolet (EUV) radiation, a form of soft x-rays, with wavelengths of 13 to 14 nm (see Fig. 3.10).

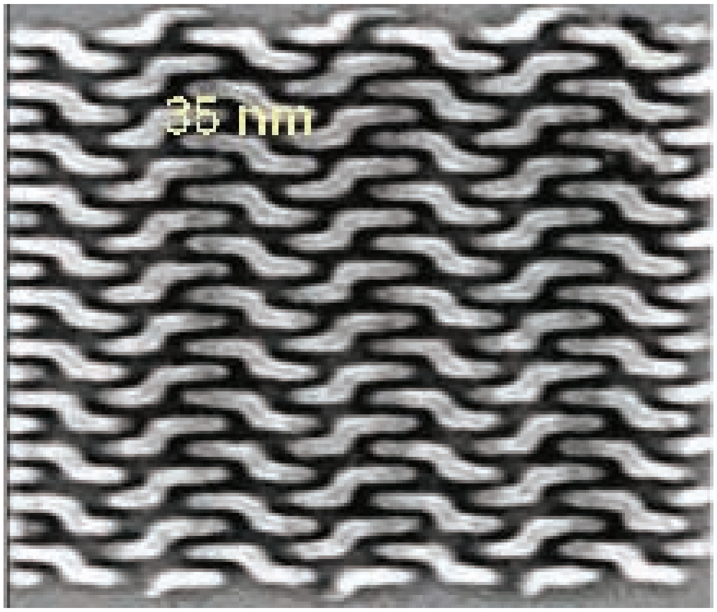


Figure 3.10. EUV exposure at 13.5 nm wavelength can create 35 nm-wide features. This work was sponsored by SEMATECH, Austin, Texas. Resist courtesy of IBM. (Photo courtesy of Patrick Naulleau, Lawrence Berkeley National Laboratory.)

The Semiconductor Industry Association, in its *International Technology Roadmap for Semiconductors*, predicts that these short-wavelength techniques will enable high-volume manufacturing of chips having 1.5 billion transistors, with leading-edge gate widths of 13 nm and clock speeds of 19 GHz [6]. Although development of related infrastructure for these capabilities, including various EUV/x-ray sources and metrologies, is in high gear, several critical capabilities are not yet resolved. Use of advanced neutron and x-ray tools in these investigations is a prime example of future opportunities related to the fabrication, processing, and measurement of novel nanoscale structures. A related example is the development of nanoscale magnetic recording structures, critically associated with national defense and commercial needs for compact information storage and retrieval. This nanotechnology is also moving towards the use of x-ray metrologies to provide essential elemental and spin-related information on a nanometer scale.

In the future, various interaction or "directing" mechanisms can be envisaged. In the near term, the development of nanometer-focusing devices will provide revolutionary tools for direct writing of features using x-ray nanobeams. The inherently short depth of field, coupled with the penetration, will allow patterns to be written at buried interfaces or line structures with high aspect ratios to be fabricated deep in the device. Looking further ahead, an even more precise technique would use the coherence of the radiation to produce standing wave patterns with nodes at the positions where specific features are desired. The resultant pattern could be used in standard etching processes or, with sufficiently high x-ray intensity from fourth-generation sources such as the LCLS, the potential pattern induced on the sample could be used to direct self-assembly of small particles.

As nanotechnology develops, the demands for high-density functionality will increase, requiring multiple functions (electric, magnetic, or optic) to be integrated into small, 3-D devices. No currently available microfabrication techniques offer easy ways to direct such assemblies. The range of dynamical interactions provided by x-ray and neutron beams could provide the solution. The interactions involved for molecular self-assembly (as used in biological systems—e.g., protein folding and formation of lipid bilayers) are typically noncovalent in nature, with energies close to thermal energies. The encounters that allow assembly are then driven by thermal agitation and, more importantly, are reversible. X-rays and neutrons can optimize the encounters that drive assembly by dynamically exciting modes. The potential is enormous; neutrons and x-rays will clearly play a catalytic role in developing high-density functional materials, devices, and systems, and in bringing forth the next generation of nanomanufacturing and processing technologies.

3.8 REFERENCES

1. P. Abbamonte, K. D. Finkelstein, M. D. Collins, S. M. Gruner, Imaging density disturbances in water with a 41.3-attosecond time resolution, *Phys. Rev. Lett.* **92**, 237401 (2004). doi:10.1103/PhysRevLett.92.237401
2. A. T. Bell, The Impact of Nanoscience on Heterogeneous Catalysis, *Science* **299**, 1688 (2003). doi:10.1126/science.1083671
3, K. A. Lokshin, Y. Zhao, D. He, W. L. Mao, H-K. Mao, R. J. Hemley, M. V. Lobanov, M. Greenblatt, Structure and dynamics of hydrogen molecules in the novel clathrate hydrate by high pressure neutron diffraction, *Phys. Rev. Lett.* **93**, 125503 (2004). doi:10.1103/PhysRevLett.93.125503
4. S. S. Ho, C. S. Yan, Z. Liu, H. K. Mao, R. J. Hemley, Prospects for large single crystal CVD diamond, *Industrial Diamond Review*, pp 28-32, (2006).
5. P. Juhás, D. M. Cherba, P. M. Duxbury, W. F. Punch, S. J. L. Billinge, *Ab initio* determination of solid-state nanostructure, *Nature* **440**, 655 (2006). doi:10.1038/nature04556
6. Semiconductor Industry Association, *The International Technology Roadmap for Semiconductors, 2005 ed.*. Austin TX: International SEMATECH (2003). www.itrs.net/Links/2005ITRS/Home2005.htm

4. ROADMAP FOR THE FUTURE OF X-RAY AND NEUTRON NANOSCIENCE

In each of the areas featured in the workshop, x-rays and neutrons play a crucial role in providing key structural and dynamic information that could lead to control over nanoscale architecture, design, and applications. However, the workshop discussions highlighted several target areas where further development of current techniques and instrumentation will be essential if the full potential of the technology is to be realized. In general, there is a need to measure smaller samples with increasing spatial and temporal resolution. This will require higher brilliance sources, improved focusing optics, faster detectors with higher spatial resolution, and novel instrumentation capable of making efficient use of the available intensities. Moreover, intelligent data acquisition systems need to be developed that allow resolution conditions to be determined by software rather than by preselection at the level of the incident beam.

A complete understanding of the hierarchical, multiscale nature of functioning nanomaterials also requires characterization over an extended range of distance and time. The structure–function relationship of a material is closely tied to the material's dynamic properties over a complex hierarchy of distance and time scales; that is, observed responses on a hierarchy of time scales do not necessarily reflect the hierarchy of distance scales. The property or function of a complex assembled nanomaterial can be characterized by a different length, or time, scale than the individual components. Unfortunately, well-understood phenomena at one length or time scale do not always translate to well-understood phenomena at another scale. Instrumental techniques will have to be developed that further extend the range of x-ray and neutron techniques to:

- image and characterize nanometer-scale structures with atomic resolution
- determine the structure of assemblies spanning from nanometers to microns
- measure very fast dynamics ranging from femtoseconds to attoseconds
- investigate slower processes with characteristic times in the range of microseconds to millisecond

The ultimate goal of providing a complete characterization of a single nanoparticle will require the combination of results from many complementary techniques. Complete characterization implies much more than a simple image, including chemical identity and positions of all atoms, magnetic structure, and tracking the dynamics of individual spins. It will require a paradigm shift in interpretation and presentation of results from scattering experiments. The development of improved methods for data sharing, real-time analysis, modeling, and visualization will provide a crucial initial step to meet this challenge.

Finally, the penetrating nature of neutrons and x-rays must be fully exploited to investigate the interior of materials in production environments, monitoring production and assembly processes under real, dynamic conditions. This can be accomplished either by taking prototyping equipment to the scattering source or by developing local sources and highly adapted scattering instruments for use at industrial plants. Pushing environmental conditions in the laboratory to extremes of temperature and pressure will not only enable simulation of current real-world production processes but will also allow access to completely new realms for controlled materials synthesis.

To meet the goals specified for the research target areas, we propose developing a prioritized instrument development program that addresses the following major themes:

- characterization in the femtosecond and attosecond time domain *(Ultrafast Dynamics)*
- investigating the relationship of structure and dynamic in hierarchical assemblies *(Bridging From Nano to Micro)*
- imaging and characterization of single nanoparticles with subnanometer resolution *(Single-Particle Characterization)*
- *in situ* measurements in a wide range of environments *(Real Environments)*
- improved data management, analysis, modeling, simulation, and visualization software to enable measurements from different techniques to be combined into a complete analysis *(Cyberinfrastructure)*

These broad, encompassing themes must be supported by concomitant programs to develop sources, instrumentation, detectors, optical components, sample environments, analysis methods, and software. Ongoing programs in some of these areas are poised to produce scientific breakthroughs in the next 5 years; other developments are still in the embryonic stage and will require further research, evaluation, and testing to achieve their full impact on nanoscience research.

Development priorities in the near term (0 to 5 years), the medium term (5 to 10 years), and beyond are presented in the following sections, and represented graphically in Figure 4.1.

4.1 ULTRAFAST DYNAMICS

The goal in ultrafast dynamics is to study chemical bonds, catalytic reactions, and magnetic switching in real time by extending measurable time scales into the femtosecond and attosecond regime. In the near term, the principle tool for ultrafast studies will be subfemtosecond x-ray sources such as the free electron laser (FEL). Concurrent development of time-stamping imaging methods (such as x-ray photon correlation spectroscopy) and ultrafast detectors must be given high priority. In the longer-term, development of energy recovery linacs (ERLs) and deep inelastic neutron scattering techniques will further advance our capabilities to probe ultrafast dynamics. ERLs will extend many standard x-ray techniques to femtosecond time scales, while neutron scattering will provide complementary information on atomic motions with attosecond time resolution.

The most significant needs are:

- development of a brilliant source of subfemtosecond x-ray pulses (FEL) (0-5 years)
- development of time-stamping techniques (0-5 years)
- creation of fast, megapixel x-ray detectors (0-5 years)
- development of instrumentation for deep inelastic neutron scattering (5-10 years)
- extension of free electron laser sources to the soft x-ray and VUV regime (5-10 years)
- further development and implementation of brilliant ERL sources (10 years+)

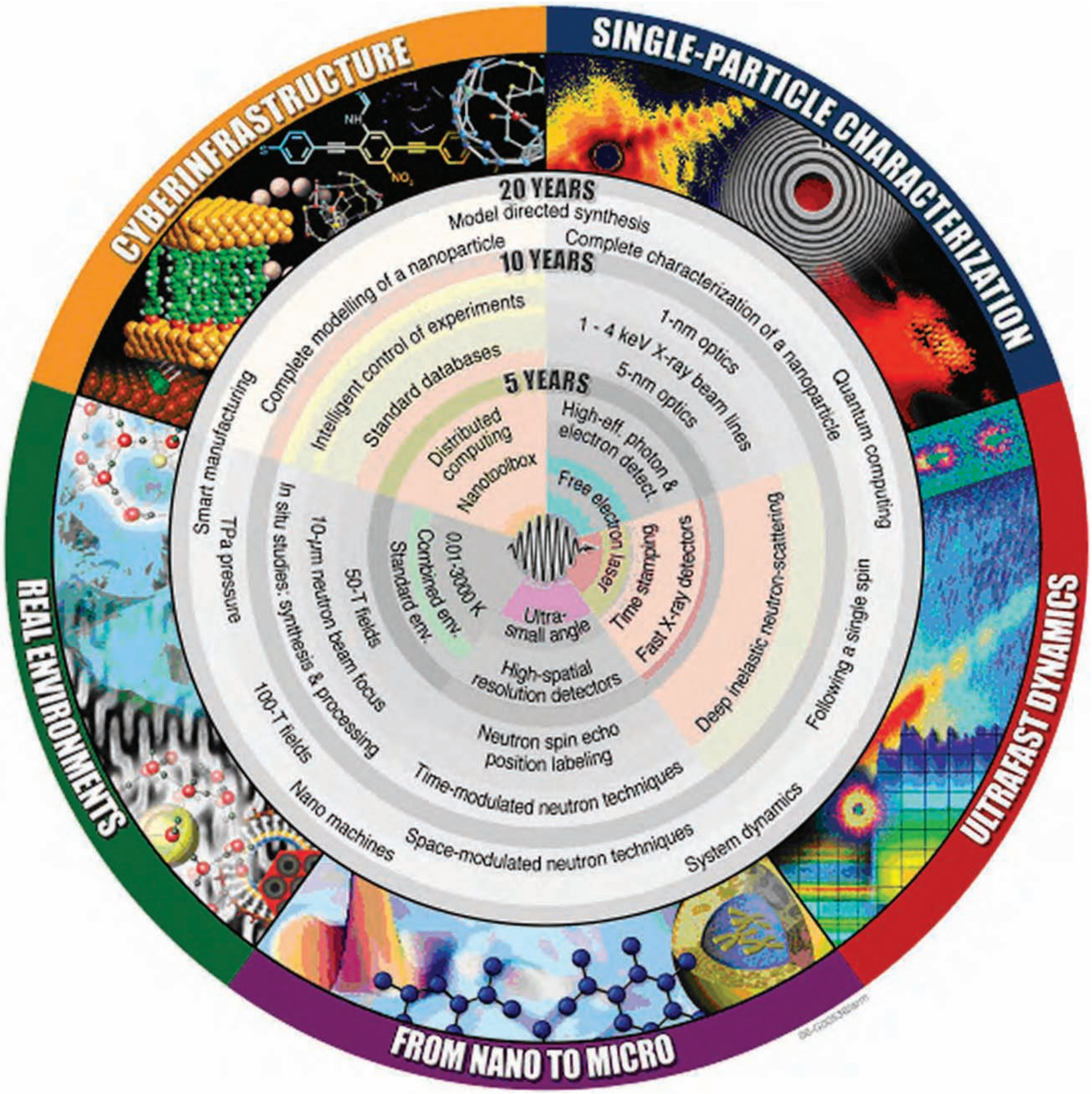


Figure 4.1. Roadmap for development of x-ray and neutron techniques for use in nanoscience and nanotechnology. Needs are positioned according to the research area or areas where they will provide the most benefit. (Courtesy of Oak Ridge National Laboratory).

4.2 BRIDGING FROM NANO TO MICRO

Nature has taught us that the structure and dynamics of hierarchical assemblies often determine ultimate function. To predict and control function, we therefore require new techniques that extend structural measurements from nanometers through to micrometers while simultaneously elucidating the characteristic dynamics (typically in the range of microseconds to milliseconds). Near-term implementation should target ultrasmall-angle x-ray and neutron instrumentation and neutron spin echo techniques. Continued development of techniques using time or space modulation of neutron beams could significantly improve measurement capability.

Important needs in this area include:

- implementation of ultrasmall-angle instrumentation (0-5 years)
- development of fast, high-spatial-resolution detectors (0-5 years)
- implementation of NSE position-labeling instrumentation (5-10 years)
- development of time- and space-modulated neutron techniques (5-10 years)

4.3 SINGLE-PARTICLE CHARACTERIZATION

To completely describe a single nanoparticle through x-ray measurements, one must focus a beam down to nanometer dimensions and apply multiple techniques. The structure of the nanoparticle can be obtained from a combination of diffraction and direct imaging using high-resolution lenses or highly coherent beams, while its chemical composition can be determined with trace-level sensitivity using fluorescence. The primary requirement for doing so is the development of a very high-intensity source of hard x-rays, such as a FEL, coupled to advanced focusing optics and high-efficiency detectors. Various focusing techniques, including zone plates, refractive lenses, Kirkpatrick–Baez mirror systems, and multilayer optics, or combinations thereof, are poised to achieve 1 to 2 nm resolution in the 5- to 10-year time frame. X-ray beam lines for resonant scattering and anomalous small-angle x-ray scattering in the energy range of 1 to 4 keV will complement the chemical analysis capability of soft and hard x-rays. The most essential needs in this area are the following:

- a brilliant source of ultra-coherent x-rays (FEL) (0-5 years)
- high-efficiency photon and electron detectors (0-5 years)
- 1 nm focusing optics (zone plates, mirrors, and mutilayers) (5-10 years)
- x-ray beam lines in the 1 to 4 keV energy range (5-10 years)

4.4 REAL ENVIRONMENTS

The penetrating capability of x-rays and neutrons can be exploited to characterize nanosystems under the conditions in which they function or are produced—for example, in gaseous, liquid, or solid-solution environments. The near-term priority should be to develop standard environmental cells at scattering beam lines that allow samples to be maintained under production prototyping conditions. Medium-term efforts should extend these capabilities to permit simultaneous measurements using multiple techniques in integrated environments. A medium- to long-term goal is the development of x-ray or neutron sources that permit in-the-field nanocharacterization for process control at the production plant.

Future extension of measurement capability to simultaneous extreme conditions of temperature, pressure, and magnetic field will enable the characterization and fabrication of novel materials. Development of new focusing optics will be a prerequisite, in particular for neutron measurements. Critical needs in this area include the following:

- standard environmental sample cells for prototyping, including, e.g., chemical vapor deposition, molecular beam epitaxy, catalytic reactors, reactive ion etching(0-5 years)
- extended range of temperature, pressure, and magnetic fields:
  - 0.01°K to 3000 °K (0-5 years)
  - 50 tesla fields, (0-5 years)
  - 100 tesla fields (5-10 years)
  - terapascal pressure (5-10 years)
- neutron beam focusing to 10 µm (5-10 years)
- in-field x-ray and neutron sources for *in situ* characterization during fabrication and processing (5-10 years)

4.5 CYBERINSFRASTRUCTURE: PUTTING IT ALL TOGETHER

The complete characterization of a functional nanomaterial is a multiscale, multidimensional problem requiring the combination of data from multiple sources, together with rapid modeling and simulation capability. X-ray and neutron techniques are often thought of as complicated. Priority should be given to developing appropriate software and hardware to simplify (or demystify) them—an x-ray/neutron cyberinfrastructure that leverages world-class computing capability to allow rapid access to shared data sets in standard formats and includes an analysis and visualization software toolbox for nonexpert users. Moreover, there needs to be an integration and coordination of data sets and analysis packages with other experimental techniques, such as electron and optical microscopy, analytical chemistry, surface analysis, and ultra-fast spectroscopy. In the medium term, online real-time utilization of these tools will enhance experimental capabilities through intelligent control. Essential cyberinfrastructure needs include the following:

- development of standard databases (0-5 years)
- creation of the Nano Toolbox (0-5 years)
- implementation of distributed computing (0-5 years)
- implementation of intelligent control of experiments (5-10 years)

4.6 BEYOND THE NEXT TEN YEARS

Any prediction we could make of the impact of nanotechnology on major issues that occupy the world today—health, energy, climate—would surely be wrong. But the overall directions are clear: nanotechnology is poised to revolutionize the world in the same way computers have over the last 50 years. Successful completion of the roadmap outlined previously will allow researchers to completely characterize single nanoparticles and to model or predict the structure and dynamical response of assembled systems. These are foundational capabilities for one of the ultimate goals in nanotechnology: functionality by design. The vision for the future is to completely model and design a functional nanosystem using the cyberinfrastructure, and then to direct its assembly and implementation using ultrahigh-precision manufacturing techniques.

Materials scientists will be able to design and build a full range of new materials, from thin films and devices to bulk functional materials, the properties of which will be defined by design at the nanoscale. We will be able to design and selectively deliver new drugs by mimicking nature. We can imagine combining nanoscale imaging capabilities with directed assembly and delivery of nanoparticles to identify and repair or eliminate specific malfunctioning cells or cell components. Future computers, and the way we interact with them, will be driven by advances in nanotechnology. Coherent x-ray beams could be used to build quantum dot computers, connected by self-assembled nanowires. These computers could be integrated into nanodevices, whose function could be preprogrammed or determined at implementation.

In conclusion, the roadmap detailed here can provide a key foundation for the nanotechnology revolution. Continued development of extremely high-intensity sources of x-rays and neutrons, and the associated instrumental techniques, is crucial. Although the high-level goals and needs mentioned here will certainly evolve over the coming decades, it is clear that x-rays and neutrons will be critical in realizing the full potential of the rich field of nanotechnology.

5. CONCLUSIONS

Recent remarkable achievements in nanoscience and nanotechnology have opened a new world of possibilities in a frontier that often appears unlimited. This promising field of study is at a pivotal point, where full exploration of its potential is closely tied to the development of dedicated synthetic and analytical techniques that enable us to produce and examine the atomic, magnetic, and electronic structure of new nanoscale materials. Although these techniques include many methods, x-ray and neutron techniques offer unique, yet complementary capabilities that are essential to reaching the ultimate goal of a comprehensive understanding of the properties of nanomaterials, structures, and devices over a wide range of length scales and time domains.

Discussions at this workshop made clear that further development of x-ray and neutron techniques and instrumentation is critical to fully realizing the potential of nanotechnology. Seven target areas were pinpointed as the most important and most promising. In general, there is a need to measure smaller samples with increasing spatial and temporal resolution and under real, or even extreme, conditions. In addition, achieving a complete understanding of the hierarchical, multiscale nature of functioning nanomaterials will require characterization over an extended range of distance and time. As nanotechnology develops, the demands for high-density functionality will increase, requiring multiple functions (electric, magnetic, or optic) to be integrated into small, three-dimensional devices. To date there are no microfabrication techniques that offer easy ways to direct such assemblies. The range of dynamics interactions provided by x-ray and neutron beams could provide the solution. Success in meeting the goals specified in the research target areas will depend on implementation of a prioritized instrument development program that addresses the following areas, detailed in Section 4, “Roadmap for the Future”:

- measurements extending into the femtosecond and attosecond time domain
- measurements covering dynamical processes with characteristics times between microseconds and milliseconds
- imaging and characterization of single nanoparticles with atomic resolution
- structural measurements covering the hierarchy of assemblies between a few hundred nanometers and several microns
- *in situ* measurements in a wide range of environments
- improved data management, analysis, modeling, simulation, and visualization software to enable measurements from different techniques to be combined into a complete analysis

In this report, we have tried to present a comprehensive picture of the current use of x-ray and neutron techniques in nanoscience and, more importantly, a vision for the future. To make the most of what nanoscale science and technology can teach us, a solid plan and dedicated effort will be required to ensure that the necessary facilities, components, and tools are available to a broad expanse of the scientific community.

APPENDIX A. ABSTRACTS

Water in Nanotubes: A New Phase of Water?

Dirar Al Homouz, George Reiter, Christian Burnham[1], Jerry Mayers, T. Abdul-Redah[2], Phil Platzman[3], Alexander Kolesnikov[4]

[1]University of Houston
[2]Rutherford-Appleton Laboratory
[3]Bell Labs Lucent Technologies
[4]Argonne National Laboratory

Deep Inelastic Neutron Scattering (DINS) from Hydrogen (or other light nuclei) can be used to measure momentum distributions. The availability of sources of high energy neutrons and improvements in data fitting methods [1,2] enable us to measure the anharmonic details of the momentum distribution, and in some cases, the Born-Oppenheimer potential of the particle. Quasi-one-dimensional water encapsulated inside single-walled open-ended carbon nanotubes, here referred to as *nanotube-water*, was studied by neutron scattering at different temperatures. [3] The system is regarded as a model system for the study of the transport of water in biological pores. The earlier results revealed an anomalously soft dynamics characterized by pliable hydrogen bonds and large-amplitude motions of the hydrogen. We have used DINS to examine the momentum distribution of the protons in nanotube water. We find that the protons are delocalized to such a degree at low temperatures (4 °K) as to qualitatively change the nature of the hydrogen bonds, to the extent that we appear to be seeing a new phase of water, while at higher temperatures (268 °K) the bonds resemble that of bulk water but are much more strongly anharmonic[4] .

References

1. R. Silver, G. Reiter, Measurement of interionic potentials in solids using deep-inelastic neutron scattering, *Phys. Rev. Lett.* **54**, 1047 (1985). doi:10.1103/PhysRevLett.54.1047
2. G. Reiter, J. Mayers, J. Noreland, Momentum-distribution spectroscopy using deep inelastic neutron scattering, *Phys. Rev. B* **65**, 104305 (2002). doi:10.1103/PhysRevB.65.104305
3. A. I. Kolesnikov, J. Zanotti, C. Loong, P. Thiyagarajan, A. P. Moravsky, R. O. Loutfy, C. J. Burnham, Anomalously soft dynamics of water in a nanotube: a revelation of nanoscale confinement, *Phys. Rev. Lett.* **93**, 035503 (2004). doi:10.1103/PhysRevLett.93.035503
4. G. Reiter, C. Burnham, D. Homouz, P. M. Platzman, J. Mayers, T. Abdul-Redah, A. P. Moravsky, J. C. Li, C.-K. Loong, and A. I. Kolesnikov, Anomalous behavior of proton zero point motion in water confined in carbon nanotubes, *Phys. Rev. Lett.* **97**, 247801 (2006). doi:10.1103/PhysRevLett.97.247801

Structure and Dynamics of Magnetic Nanoparticle Assemblies

Meigan Aronson, University of Michigan

Advances in synthetic techniques have made available large quantities of monodisperse magnetic particles and molecular moieties which can be subsequently assembled into extended structures. Different aspects of the functionality of these confined magnetic entities can be addressed ranging from applications and devices, to the construction of model magnetic systems for fundamental studies. In each case, a wide range of experimental techniques must be brought to bear, including synthesis, visualization, magnetic functionality, and ultimately scattering studies of the magnetic structure and dynamics. Particularly challenging for scattering measurements is the need to determine structure on length scales which range from the unit cell to the particle dimensions and on to the correlation scale within the assembly of nanoparticles. Similarly, studies of the dynamics must be carried out on energy scales matched to these very different length scales, spanning intraparticle spin waves, particle reorientation and precession, and the collective excitations of the assemblage. New instrumentation is required to meet these challenges.

The Grand Challenges in Nanomagnetism*

S. D. Bader, Argonne National Laboratory

Synchrotron x-ray facilities [1] and neutron scattering facilities [2] provide boundless opportunities to explore new nanomagnetic materials and phenomena. This talk provides an overview of the grand challenges in nanomagnetism. Examples of the use of x-rays and neutrons to explore and understand exchange coupling phenomena across interfaces of magnetic films, multilayers and laterally confined structures are provided [3-7]. The fundamental scientific problems involve the need to understand the nature of confined spin states, ultra-fast spin dynamics, and novel spin transport [8]. *This work was supported by DOE-BES, under contract W-31-109-ENG-38.

References

1. J. B. Kortright, D. D. Awschalom, J. Stöhr, S. D. Bader, Y. U. Idzerda, S. S. P. Parkin, I. K. Schuller, and H.-C. Siegmann, Research frontiers in magnetic materials at soft x-ray synchrotron radiation facilities, *J. Magn. Magn. Mater.* **207**, 7-44 (1999). doi:10.1016/S0304-8853(99)00485-0
2. M. R. Fitzsimmons, S. D. Bader, J. A. Borchers, G. P. Felcher, J. K. Furdyna, A. Hoffman, J. B. Kortright, I. K. Schuller, T. C. Schulthess, S. K. Sinha, M. F. Toney, D. Weller, S. Wolf, Neutron scattering studies of nanomagnetism and artificially structured materials, J. *Magn. Magn. Mater.* **271**, 103-146 (2004). doi:10.1016/j.jmmm.2003.09.046
3. D. Haskel, G. Srajer, J. C. Lang, J.Pollmann, C. S. Nelson, J. S. Jiang, S. D. Bader, Enhanced interfacial magnetic coupling of Gd/Fe multilayers, *Phys. Rev. Lett.* 87, 207201 (2001). doi:10.1103/PhysRevLett.87.207201
4. D. Haskel, G. Srajer, Y. Choi, D.R. Lee, J.C. Lang, J. Meersschaut, J.S. Jiang, S.D. Bader, Nature of inhomogeneous magnetic state in artificial Fe/Gd ferrimagnetic multilayers, *Phys. Rev. B* **67**, 180406(R) (2003). doi:10.1103/PhysRevB.67.180406
5. K. Buchanan, V. Novosad, K. Yu. Guslienko, A. Doran, A. Scholl, S. D. Bader, Magnetization reversal in patterned double-vortex structures, *J. Appl. Phys.* **97**, 10H503 (2005). doi:10.1063/1.1855207
6. C. L'abbé, J. Meersschaut, W. Sturhahn, J. S. Jiang, T. S. Troellner, E. E. Alp, and S. D. Bader, Nuclear resonant magnetometry and its application to Fe/Cr multilayers, *Phys. Rev. Lett.* **93**, 037201 (2004). doi:10.1103/PhysRevLett.93.037201
7. S. G. E. te Velthuis, J. S. Jiang, S. D. Bader, G. P. Felcher, Spin flop transition in a finite antiferromagnetic superlattice: Evolution of the magnetic structure, *Phys. Rev. Lett.* **89**, 127203 (2002). doi:10.1103/PhysRevLett.89.127203
8. Y. Ji, A. Hoffmann, J. S. Jiang, S. D. Bader, Spin injection, diffusion, and detection in lateral spin-valves, *Appl. Phys. Lett.* **85**, 6218 (2004). doi:10.1063/1.1841455

A Time Lens for High Resolution Neutron Time of Flight Spectrometers

K. Baumann[1]*, R. Gähler*[2]*, P. Grigoriev*[2,3]*, E.I. Kats*[2,3]

[1]Technische Universität München

[2]Institut Laue Langevin

[3]L.D. Landau Institute for Theoretical Physics

We are currently studying the imaging effects of temporal neutron lenses. Our lens is based on a traveling non-homogeneous magnetic field with parabolic shape which is analytically determined and numerically verified by appropriate calculations. The lens is intended to replace the traditional chopper system used for time of flight instrumentation to enhance intensity and/or time resolution significantly. A first estimation of the gain factor points to a value of 5.5 with a time resolution of 5 µs which is hardly achieved by traditional systems. The proposed experimental setup seems to be feasible and may open new fields of applications regarding to high resolution spectrometry. The contribution starts with the basic ideas and methods applied. Some of these ideas are already published but have never been aimed to study a time lens for neutron time-of-flight spectrometers. Further, we will discuss possible design parameters and miscellaneous subjects related to time lens focusing such as aberration. We conclude with results from numerical calculations that, for example, provided us a view of the evolution of the phase space element during propagation through the optical system.

Atomic Imaging by Fourier Inversion of X-ray Standing Wave Data

Michael J. Bedzyk, Northwestern University

The need to understand the structure–property–processing relationships for various interface-based nanoscale materials systems strongly motivates the development of new *in situ* experimental techniques for directly observing structures at the atomic-scale. The relevant processing environments may vary from vacuum, as in the case of oxide/semiconductor molecular beam epitaxy, to liquid, as in the case of biomolecular adsorption. While scanning-probe-microscopy-based techniques partially fulfill this demand by giving a top-view of a given structure, it is important to fill in the entire top-to-bottom in-depth view with quantitative, element-specific, structural information for describing the atomic arrangements, including for example, the electronic and magnetic states of atoms within the arrangement. This is a challenge for developers of x-ray scattering and spectroscopy techniques.

A crucial problem facing scattering measurements is in transforming the reciprocal space data into real-space images. This is primarily due to the "phase problem", which in a growing number of cases can be circumvented by using a reflection generated x-ray standing wave (XSW) as a spectroscopic probe. The XSW technique measures the amplitudes and phases for element-specific atomic distributions. As recently shown, the summation of these Fourier components produces a model-independent 3-D atomic map of each x-ray-fluoresence specified atom with a $1/Q_{max}$ spatial resolution. While XSW atomic imaging has thus far have been restricted to XRF detectable atoms for element sensitivity, it should be extended to other spectroscopy channels, e.g., XPS for chemical sensitivity and circular magnetic dichroism for magnetic sensitivity.

In addition to XSW measurements, other pieces of the puzzle can be filled in by applying other scattering and spectroscopy techniques, such as surface extended x-ray absorption fine structure for determining bond lengths, x-ray photoelectron spectroscopy for determining the chemical bonding states, and x-ray reflectivity for studying molecular packing. For reliability it is important in many cases to make as many of these measurements on the same sample, in the same environment, in a reasonably short time-frame. This calls for multitasking experimental stations that combine x-ray scattering and spectroscopy into one integrated system.

Important areas to be studied by this combined scattering and spectroscopy approach include silicon-based molecular electronics, biomolecular attachment to functionalized surfaces, multifunctional oxide epitaxy, and supported metal oxide catalysts.

The Nanostructure Problem

Simon J. L. Billinge, Michigan State University (MSU)

Structure is fundamental to materials properties. Revolutions in materials science and molecular biology followed rapidly from the ability to obtain atomic scale structure using crystallography. The structure of periodically arrayed nanoparticles can be solved, as in the case of protein crystallography; however, crystallography fails for discrete nanoparticles and disordered ensembles of particles.

By definition, nanoparticles are not periodically long-range ordered. As a result, sharp Bragg peaks broaden into diffuse features that often overlap each other resulting in a loss of information in the data. On the other hand, the structure of the nanoparticles in general is complex and requires many unique atomic positions to be specified. Robust structural solutions of complex nanoparticles are difficult or impossible—this is the nanostructure problem.

Some progress has been made using total scattering methods such as the atomic pair distribution function method which yields weighted distributions of inter-atomic distances. In this case, structure refinement of reasonable initial models is often possible; however, *ab initio* structure solution of an unknown structure has not been demonstrated. Other techniques, such as EXAFS, NMR, TEM, and other imaging techniques are also brought to bear and provide complimentary information. However, in general, using data from any single technique, the nanostructure problem is not well conditioned. There is not a good balance between information content in the data and degrees of freedom in the model and resulting models are not unique (often far from it). A robust solution to the nanostructure problem requires that it is recast in a well-conditioned way such that the data constraints are greater than the degrees of freedom in the model. This will likely require a concerted effort to combine self-consistent data from multiple complementary techniques with a software development effort in order to handle the diverse data as well as combine modeling and regression in a self-consistent optimization. Research on this topic is underway at MSU funded by a DOE-BES II grant.

What is needed is the following:

1. beamlines in close proximity with a flexible access structure that allows the complementary data to be collected quickly without multiple trips and proposals, including the following technique:
    (a) PDF
    (b) EXAFS
    (c) NMR
    (d) anomalous scattering
    (e) high-intensity neutron powder diffraction
    (f) microbeam diffraction
    (g) TEM/electron diffraction
    (h) imaging techniques (scanning probe, diffraction/nanoprobe imaging)

2. data analysis software development in cooperation between theorists and experimentalists
3. computing software and hardware support that is x-ray/neutron-facility-independent but adequately funded

Synthesis and Characterization of Novel Polymer Architectures

Phillip F. Britt, Oak Ridge National Laboratory

One of the greatest challenges facing chemistry, physics, and materials science today is the controlled synthesis of mesoscopic materials (i.e., materials with characteristic dimensions of 1-100 nm) with well-defined structures and properties, and the assembly of these materials into macroscopic functional devices. One approach that has generated significant interest has been the "bottom-up" approach, used by nature, which starts with single molecules of controlled size, shape, and functionality (such as amino acids) and assembles them through covalent and/or noncovalent interactions into functional supramolecular assemblies (such as enzymes). The ultimate goal is to develop reproducible synthetic methods, which controls interfacial interactions, defects, composition, and structure, to produce materials that possess the desired function or property via an understanding of the nanoscale physics and chemistry. To achieve this goal, a better understanding is needed of the thermodynamic and kinetic processes (such as self-assembly) at the nanoscale and a better understanding is needed of structure–property relationships at all length and time scales. Characterization tools are also needed to observe and characterize events at the nanoscale in real time and under a variety of environments (such as temperature, pressure, and shear). Since small angle scattering techniques using either x-rays or neutrons provide statistically averaged structural information on length scales of 1-100 nm, these tools are ideally suited to study structure and dynamics of hard and soft materials (including polymers, copolymers, biomaterials, composites, micelles, colloids, mesoporous metal oxides, magnetic materials, metallic alloys, etc.) and interfaces. The high penetrating power of neutrons also allows studies to be conducted in concentrated solutions and in the bulk. The large difference in scattering length of neutrons for hydrogen and deuterium provides a unique opportunity to manipulate the contrast without changing the structure. Thus, neutrons are ideally suited to study the molecular conformation and interactions of polymer chains in the bulk, in blends, in dilute solution, and at interfaces under a variety of conditions such as shear or deformation at controlled temperatures and pressures. Nevertheless, new developments are still needed in developing sample environments to study smaller samples at finer spatial resolution (1 nm), and to make real-time measurements. New methods are also needed to obtain 3-D images of complex nanostructured materials to truly understand structure–properties relationships at the nanoscale. This presentation will highlight some of the synthetic advances made in polymer science, the complex molecular architectures that can be made, and the opportunities to use x-rays and neutrons to provide new insight into the rule governing nanoscale chemistry and physics.

Impact of a Future Energy Recovery Linac X-ray Source on Nanoscale Science

*Joel D. Brock,*Cornell University*

The performance characteristics of modern third-generation synchrotron x-ray sources are approaching fundamental physical limits set by the equilibrium dynamics of particle storage rings. Even in the absence of interactions, the orbit of a single charged particle varies with the energy of the particle as it emits photons and then is re-accelerated by the radio frequency (RF) cavities. Over many revolutions (or equivalently, in an ensemble of many particles), a finite phase space distribution that is much broader in the plane of the storage ring than perpendicular to the plane develops. This fundamental effect does not, however, apply to the electron beams in linacs because the time scale required to achieve the equilibrium distribution is orders of magnitude longer than the transit time. In an energy recovery linac each particle is accelerated by the RF cavities in a linac, transits a brilliance preserving loop instrumented with insertion devices, and is then de-accelerated by the same linac. Each particle suffers only minute changes in energy. The de-acceleration process returns the particle's energy to the RF cavity with essentially zero loss. The energy recovery linac is an energy storage rather than a particle storage device. Without energy recovery, a linac x-ray source would be prohibitively expensive to operate.

Detailed designs developed by Cornell University's ERL prototype project demonstrate that an ERL would be a fully diffraction-limited x-ray source for photon energies less than or equal to 12.6 KeV and with a (circular) emittance of 0.008 nm-radians. These parameters imply 1-10 nm circular beam waists for focused x-ray beams but with intensities comparable to current third-generation synchrotron beam lines. Such an x-ray source would enable the application of essentially all existing x-ray characterization techniques to individual nanoparticles (e.g., 20-50 nm). For example, fluorescence detection and spectroscopy of individual impurity atoms would become possible. A variety of ultra-fast (sub-picosecond) and coherent x-ray imaging techniques also would become possible.

* on behalf of the ERL team of I. V.Bazarov, S. Belomestnykh, D. Bilderback, J. D. Brock, E. Fontes, K. D. Finkelstein, S. M. Gruner, G. Hoffstaetter, A. Kazimirov, M. Liepe, Y. Lin, H. S. Padamsee, D. Sagan, V. Shemelin, Q. Shen, K. Smolenski, C. Sinclair, R. Talman, M. Tigner, V. Veshcherevich, Cornell University; and L. Merminga & G. Krafft of Thomas Jefferson Lab National Accelerator Facility.

Relevance of Strong Electronic Correlations in Bulk and Nano Systems

Elbio Dagotto, University of Tennessee and Oak Ridge National Laboratory

The study of strongly correlated electronic (SCE) systems is among the most popular areas of investigations in condensed matter physics. The reason is that these materials have provided conceptually unexpected phenomena such as high temperature superconductivity and colossal magnetoresistance. In recent years, a large effort both in theory and experiments has shown that materials of this variety tend to have self-organization effects at the nanoscale, often crucial to microscopically understand the bulk behavior they present. Neutron and x-ray studies have been fundamental to reveal these nontrivial electronic structures, unveiling a complex behavior similar to that observed in soft matter. Transferring this knowledge to nanosystems, such as conductors involving small molecules where charging effects are important, or quantum dots with the Kondo effect, or long molecules with polaronic formation, is a frontier that it is barely explored.

I will argue that a research effort focused on the analysis of similarities between bulk and nano involving SCE materials is very important, particularly for the plethora of new concepts that may emerge, and that the natural physical location for such efforts is at DOE laboratories where large scattering facilities are close to nanocenters.

Atomic Structure of Materials with Nanoscale Coherence

T. Egami, University of Tennessee and Oak Ridge National Laboratory

Nanoscale materials, such as nanoparticles, are usually characterized by their size, assuming that their atomic structure is the same as in the bulk. However, for complex materials, which are increasingly gaining attention as functional materials, this assumption is often false. Confinement to the nanoscale can make competing phases more stable, and nanoparticles can have metastable or unstable atomic structure which can produce unusual and attractive properties. Conventional crystallographic methods of structural characterization are powerless for such materials, and local methods emerge as more effective alternatives. We describe one of these methods, the atomic pair-density function analysis of static as well as dynamic structure at a nanoscale, using pulsed neutrons and synchrotron x-rays as a probe.

Can Kinoform Hard X-ray Optics Produce Sub-10-nm Beams?

Kenneth Evans-Lutterodt, Brookhaven National Laboratory

Based on our experience with, and understanding of, the refractive and diffractive properties of kinoform lenses, we extrapolate beyond current practical limitations and try to understand possible limiting behavior of this type of focusing optic. Kinoform Fresnel lenses have lower absorption and larger apertures than the equivalent refractive-limit lens. This leads to optics with smaller focused spots, but at the expense of choosing to operate these lenses at or near a fixed design wavelength. Using microfabrication techniques, we have manufactured low-loss kinoform Fresnel lenses for hard x-rays at energies of 11.3keV, and energies as high as 30keV. We present measurements and simulations of the effectiveness of kinoform lenses and discuss the possibility of sub-10-nm focused beams. Research carried out at the National Synchrotron Light Source under DOE Contract No. DE-AC02-98CH10886.

Characterization of Soft Nanostructured Materials

Millicent A. Firestone, Argonne National Laboratory

The control of self-assembly, the process by which order arises from a collection of disordered molecules or objects, to achieve functional nanoscale materials that could provide the basis of nanoscale devices (e.g., switches, gates, or memory elements) remains a significant challenge and constitutes a major goal in the field of nanoscience. Unlike top-down fabrication approaches, self-assembly offers the potential of preparing nanoscale materials in an inexpensive, low-energy consumption, “multiple copy” fashion. In addition, the self-assembly of molecules provides a means by which to pattern functional nanostructures with feature sizes not achievable via lithographic approaches and to construct patterned 3-D structures. Although a considerable amount of effort has been directed towards the study of self-assembly, few guiding principles for the *de novo* design of functional self-assembled nanostructures have emerged. The lack of a directed/rational approach to achieving functional, self-assembled materials is the result of both the complexity of the objects and forces that control the self-assembly process and the limitations of the techniques now available for the characterization of self-assembled soft materials. Thus, improving the characterization of static, dynamic, and *in situ* self-assembly remains a current and significant challenge in nanoscience.

Although the development of scanning probe / microscopy techniques has yielded notable advances in nanoscale characterization of materials, the study of soft materials such as complex fluids with these techniques is not possible without altering or perturbing the samples. X-ray and neutron scattering techniques therefore remain the preferred approach to study such systems, since they can probe structure on the mesoscopic (nanometer to micron) length scale and can probe bulk phase materials in a non-perturbing, non-destructive way under realistic sample environments (e.g., high levels of hydration). X-ray and neutron scattering techniques such as small-angle, ultra-small-angle, and grazing incidence x-ray scattering as well as reflectivity can be used to determine structure under controlled environmental conditions (e.g., under the influence of applied electric or magnetic fields) and to monitor the *in situ* self-assembly process. Neutrons offer the additional advantage of characterizing low-Z element compositions via the use of isotopic substitution and contrast matching. Current approaches, however, provide low to medium resolution structure determination in reciprocal space. Improvements are needed to further increase the structural resolution and to be able to achieve this in one, two and three dimensions. A major advancement would be the development of experimental approaches to provide real-space imaging, such as those obtained by scanning probe methods. For example, 3-D tomography would yield high resolution images of soft materials and would represent a significant advance over current capabilities, bridging the gap between electron microscopy and optical microscopy. Lastly, due to the diversity of interactions among molecules, a true understanding of self-assembly will require probes that are sensitive to both local and extended structure over a wide range of spatial and temporal dimensions. Such information may only be provided by coupling scattering techniques with standard spectroscopic methods.

Nanostructured Magnetic Materials: Novel Physics and Emerging Technologies

Eric E. Fullerton, Hitachi Global Storage Technologies

Magnetic storage has played a key role in audio, video, and computer development since its invention more than 100 years ago. In 1956 IBM built the first magnetic hard disk drive featuring a total storage capacity of 5 Mbytes at a recording density of 2 kbits/in^2. Since then the density of bits stored on the surface of a disk has increased to 100 Gbits/in^2, with data rates approaching a GHz. At such densities, the bits must be positioned on the disk with nanometer resolution. In the magnetic recording industry (and similarly in the semiconductor industry) increased capacity and performance was historically achieved by scaling the critical device dimensions. While this approach has been the basis for much of the 50-million-fold increase in disk drive capacity, it appears to be reaching limits. These limits arise from difficulties in lithography and, more fundamentally, because of materials limitations. In current devices, most of the critical dimensions are now in the nanometer range where two issues become critical. The first is that surface and interface effects dominate over bulk material properties. The second is the thermodynamic properties of small structures and the increasing importance of thermal energy. The superparamagnetic limit in recording media is a prime example of the latter where the magnetic energy of nanoparticles becomes comparable with k_BT.

Continued growth of storage densities will require the development and characterization of new nanostructured materials and architectures that control magnetic interaction and correlations on the nanometer scale and exploit the unique physics that emerge at the nanoscale. In general, much of the new physics comes from combining disparate materials (ferromagnets, antiferromagnets, paramagnets, insulators, etc.) on nanometer scales. The magnet response of the composite often provides exciting new scientific questions as well as the impetus for emerging technologies. The classic example is giant magnetoresistance, originally discovered in iron–chromium superlattices, where the measured magnetoresistance was two orders of magnitude greater than that expected for iron films. While GMR is currently used in all hard drives and has led to the general field of spintronics, it is just one example of the complex magnetic phenomena that can occur at the nanoscale. Other phenomena such as interlayer exchange coupling, exchange biasing, and exchange spring magnets also provide unique functionality at the nanoscale, and will be highlighted.

Neutrons and Nanoscience – Some Scientific and Instrumental Perspectives

R. Gähler, Institut Laue Langevin

We estimate the length- and time-scales, which are accessible with neutrons from present sources, and we show what can be done and what can't be done. New perspectives will emerge in reflectometry, small angle scattering, and SANS-tomography; all these techniques are based on new or recently developed experimental methods. Finally, we outline some visions, capable to open new areas for neutron science.

Probing Soft Nanostructured Interfaces with X-rays

O. Gang, Brookhaven National Laboratory

In order to understand the properties of many nanoscale materials there is a critical need for structural techniques that provide time- and depth-dependent information *in situ*. We will demonstrate how Grazing Incident Small Angle x-ray Scattering and x-ray reflectivity can be used (i) to probe the structure of self-assembled systems under environmental conditions on the 1-100 nanometers length scale, and (ii) to study the effect of liquids on nanostructured surfaces.

(i) In order to control and direct self-assembly on the nanoscale, an understanding of kinetics processes and equilibrium states are required. *In situ* structural studies on several self-assembled systems, including diblock copolymers and nanoparticles, will be presented. For dibock copolymers, hexagonally packed cylinders are formed in a specific range of the diblock's fraction and Flory interaction parameter. These cylinders may orient either parallel or perpendicular to the substrate, and the degree of crystalline order is in part controlled by the solvent concentration and film thickness. Real-time GISAXS studies, along with optical thickness measurements, provide a means of correlating the structure with the solvent concentration. In the second example, monolayers of nanoparticles, capped with organic ligands, have been investigated in the presence of ultra-thin (< 10 nm) liquid films. When the nanoparticle diameter is comparable to the solvent film thickness, the crystallinity of the monolayer is improved, regardless of the detailed solvent properties. For poor solvents, bulk nanoparticle aggregation may be induced.

(ii) Understanding wetting phenomenon on nanostructured surfaces is crucial for enabling many emerging technologies, including nanofluidic, advanced lithographic processes, and rheological applications. Recent results on wetting of nanopatterned surfaces by simple liquids will be presented. A significant enhancement of the liquid adsorption, compared to the flat surface, was detected for the filling of nanocavity with liquid. This enhancement, however, is weaker than predicted. The possible origin of this discrepancy will be discussed.

*Collaborators: M. Fukuto, A. Checco, B. Ocko, Brookhaven National Laboratory; K. Alvine, D. Pontoni, P. Pershan, Harvard University; S. Kim, M. Misner, T. Xu, T. Russell, University of Massachusetts; A. Gibaud, University de Maine (France); D. Smilgies, Cornell University

Quantum Liquids Confined to Nanoscales Explored with Neutrons

Henry R. Glyde and Souleymane Omar Diallo, University of Delaware

Neutron scattering measurements of the dynamics and structure of quantum liquids confined in nanoporous media and on surfaces has recently become possible. Porous media introduce disorder and large surface areas (2-D systems) as well as nanoscale confinement. A variety of media can be investigated: Vycor, silica gels, MCM-41, nanotubes, and flat MgO surfaces, but sample size and sample handling is always an issue. The neutron scattering measurements of dynamics include inelastic time of flight, triple axis, backscattering, and deep inelastic scattering. The elastic scattering measurements are aimed at structure determinations on surfaces. They have been made to date at the ISIS Facility, Rutherford Appleton Laboratory, UK, and at the Institut Laue Langevin, Grenoble, largely as a result of existing collaborations and sample handling facilities. Our present goals are chiefly scientific rather than direct materials development. They are:

1. to explore the interplay of Bose-Einstein condensation (BEC), the elementary (phonon-roton) excitations and superfluidity of quantum systems at nanoscales. Confinement to nanoscales and disorder modifies BEC, the excitations and superfluidity differently and therefore reveals their interdependence (1). While superfluidity has been explored for many years, neutrons are unique in their ability to reveal excitations and BEC and this has only recently begun. Helium at nanoscales is a model for other disordered Bose systems (e.g., High T_c materials, Josephson Junction arrays). It is closely related to BEC and superfluidity of alkali atoms confined in magnetic traps and in optical lattices discovered in 1995 and 2002.
4. to explore quantum liquids at negative pressures [2] and to large positive pressures [3] (metastable states in nanoconfinement).
5. to determine the shape of the atomic momentum distribution and BEC generally in quantum solids [4]and liquids.
6. to determine the structure of helium on nanotubes, and to create 1-D and 2-D quantum systems and 1-D — 2-D crossover [5].

The unique future role of neutrons in this field and opportunities opened by the combination of improved neutron facilities and new nanostructured materials will be discussed.

References

1. F. Albergamo, H. R. Glyde, D. R. Daughton, N. Mulders, J. Bossy, H. Schober, Excitations of liquid ^{4}He in disorder and boson localization, Phys. Rev. B **69**, 014514 (2004). doi:10.1103/PhysRevB.69.014514
2. F. Albergamo, J. Bossy, P. Averbuch, H. Schober, H. R. Glyde, Phonon-Roton Excitations in Liquid ^{4}He at Negative Pressures, *Phys. Rev. Lett.* **92**, 235301 (2004). doi:10.1103/PhysRevLett.92.235301
3. J. V. Pearce, J. Bossy, H. Schober, H. R. Glyde, D. R. Daughton, N. Mulders, Excitations of Metastable Superfluid ^{4}He at Pressures Up to 40 Bars,*Phys. Rev. Lett.* **93**, 145303 (2004). doi:10.1103/PhysRevLett.93.145303
4. S. O. Diallo, J. V. Pearce, R. T. Azuah, H. R. Glyde, Quantum Momentum Distribution and Kinetic Energy in Solid ^{4}He, *Phys. Rev. Lett.* **93**, 075301 (2004). doi:10.1103/PhysRevLett.93.075301
5. J. V. Pearce, M. A. Adams, O. E. Vilches, M. R. Johnson, H. R. Glyde, One-Dimensional and Two-Dimensional Quantum Systems on Carbon Nanotube Bundles, *Phys. Rev. Lett.* **95**, 185302 (2005). doi:10.1103/PhysRevLett.95.185302

Catalysis by Metal Nanoclusters

D. Wayne Goodman, Texas A&M University

The electronic, structural, and chemical properties of unsupported metal and mixed-metal surfaces prepared either as single crystals or thin films have been detailed and contrasted with the corresponding properties of metal and mixed-metal nanoclusters. The latter vary in size from a few atoms to many and have been prepared on ultrathin single crystalline oxide supports of titanium oxide (TiO_2), aluminum oxide (Al_2O_3), and silicon oxide (SiO_2). An array of surface techniques including reaction kinetics of carbon monoxide oxidation and vinyl acetate synthesis have been used to correlate catalytic function of these surfaces with their physical and electronic properties. Of special interest are the special physical and chemical properties that develop with metal cluster size reduction and/or metal-support interaction.

The Active Sites in Catalysis

Jan Hrbek, Brookhaven National Laboratory

In a broad scientific sense x-rays are an ideal probe for the study of the correlation between nanoscale structure and function. In general, the scientific questions are related to understanding the effects of finite size, local structure and confinement, and correlation of these with the unique physical/chemical properties. Diffraction and spectroscopic investigations of the atomic structure and chemical composition of nanometer-sized objects and simultaneous monitoring of chemical reactivity will lead to design of optimal materials with significant implications for the nation's energy and economic security. The ability to measure the *in situ* catalytic activity of a single nanoparticle or a nanometer-sized region of a heterogeneous catalyst and correlate that with changes in the physical and electronic structure under reaction conditions of high pressure and temperature, will revolutionize the catalysis science, leading to the possibility of rational design of catalysts.

The concept of "active sites" in heterogeneous catalysis was developed around an idea of adsorbate bond activation and breaking at specific structural arrangements of surface atoms with low coordination. The identification and characterization of such active sites is of paramount importance for the understanding of surface chemical reaction and rate limiting steps, and for the improvement of catalysts' activity/selectivity. Using the state-of the-art instrumentation and theoretical calculations, structural defects on extended surfaces (e.g., vacancies, impurity atoms, steps, kinks, dislocations, and strain) were identified as centers of locally increased chemical or catalytic activity. Currently, the catalysts and the active sites are described as static structural units. As demonstrated in several recent experiments the dynamic active sites are formed and dissolved on metal surfaces at relevant temperatures and adsorbate concentration. Experimental tolls with very high spatial, temporal, and energy resolution will have to be developed and used in combination or simultaneously to address fundamental questions of crucial importance for catalysis science. Microsecond x-ray diffraction and absorption experiments under reaction conditions, Fast high-pressure high-energy resolution photoemission, and element specific low-energy electron microscopy (LEEM) or x-ray photoelectron emission microscopy (XPEEM) with nanometer scale resolution are several examples of synchrotron-based tools that will have a great impact on future development of catalysis science.

Neutron Guides with Adiabatic Shape Transformation

Tobias Hürlimann, Institut Laue-Langevin (ILL) and student at Technical University of Munich

Using rectangular-shaped neutron guides can lead to a change in divergence which might be very unfavorable for certain instruments, for example a horizontal reflectometer. The reason is missing exchange of horizontal and vertical divergence in such guides, because all guide surfaces are perpendicular to each other. Guide with curved surfaces may provide a solution to this problem, by making exchange between horizontal and vertical divergence possible. In my talk I will present the concept of an adiabatic shape transformation guide, which was suggested by Roland Gähler (ILL, Grenoble). After demonstrating the geometry design of that special shape, I will show some Monte Carlo simulation results and talk about advantages and weak points of such a guide.

Advanced Characterization Needs for Epitaxially Grown NanoStructures

Robert Hull, University of Virginia

The epitaxial growth of two dimensional (thin layers), one dimensional (wires), and zero dimensional (quantum dot) epitaxial structures is a core field of nanoscience, particularly in semiconductor heteroepitaxy. Such structures enable confinement of electronic carriers, engineering of quantum properties, and ultimately control of electronic (charge) and magnetic (spin) properties at the single electron level. Arguably, the demands on advanced characterization methods are outstripping nanofabrication capabilities in this field. Challenges include the need to measure chemistry in extremely small structures, to understand the time evolution of structures through *in situ* methods, to determine the presence of electrically active impurities (dopants), and to measure surface and subatomic structure with atomic precision. This overview will illustrate these challenges and pose the question of what breakthrough experiments or techniques are needed in this field.

Scientific Opportunities with Synchrotron Radiation for Nanoscience

Zahid Hussain, Lawrence Berkeley National Laboratory

High brightness, tunuability, timing structure, and polarization available from modern synchrotron radiation facilities provide unique opportunities for nanoscience research. Synchrotron radiation provides the unique capabilities to perform *in situ* studie*s* of materials in real environment. Various spectroscopies available with synchrotron radiation allow the study of quantum confinement and electronic structure of materials with high resolution. Diffraction techniques provide the information for atomic structure. Time-resolved dynamic capabilities are provided by the pulsed nature of radiation as well as by the use of coherent scattering techniques. High brightness of synchrotron radiation allows focusing the beam down to 10s of nm dimension, and thus permit single nanoparticle imaging. This talk will provide information about the present state-of-the-art in synchrotron radiation instrumentation and techniques and how it is used for understanding various properties of nanostructures. The talk will also discuss new scientific opportunities in nanoscience where development of new instrumentation could play an important role.

Advanced Neutron and X-ray Focusing Optics for the Study of Nanoscale Materials

Gene E. Ice, Oak Ridge National Laboratory

With sufficient spatial resolution, x-ray diffraction and spectroscopy can provide detailed information about the composition, crystalline structure, and chemistry of individual nanoscale particles. This information is essential to understand the materials behavior of nanoscale regions embedded in larger sample volumes or surrounded by other nanoscale regions with distinct crystallographic orientation or structure. Polychromatic or nondispersive scanning methods are particularly important as they minimize problems of sample motion that are particularly serious for nanoscale research and allow for rapid determination of the local crystal structure in a small region. Similarly, advanced neutron and x-ray diffraction and spectroscopy methods form the basis for characterizing the *average* properties of nanoscale materials. Here again the ability to study small volumes is of critical importance for understanding small amounts of material prepared by novel synthesis methods. The use of polychromatic neutron techniques is particularly important for small sample volumes; polychromatic techniques efficiently use more neutrons to maximize the signal from small, weakly-interacting samples.

Fortunately, the ability to efficiently focus polychromatic/wide bandpass neutron and x-rays beams to small sizes is undergoing a revolution. This revolution, combined with the matching 3-D resolution offered by differential aperture microscopy, will greatly extend the kinds of nanoscale materials that can be studied with neutrons and x-rays from major synchrotron and neutron facilities. For example, high-performance neutron supermirrors can now focus polychromatic neutron beams to ~0.01-0.001 mm^2 with brilliance approaching the theoretical limit determined by the source. This allows for the application of advanced neutron diffraction and spectroscopy experiments to very small sample volumes with good signal-to-noise. Nondispersive Kirkpatrick-Baez x-ray mirrors can similarly now focus beams to ~40 to 100 nm, which allows for spectroscopy and diffraction studies of individual nanoscale regions within larger sample volumes. Even more advanced focusing methods are emerging with the potential to produce x-ray beams with spot sizes near 10 nm and with the ability to produce neutron beams with sufficient intensity to characterize sample volumes less than 10^{-6} mm^3. We discuss these developing methods and their applications to nanoscale research.

Understanding Magnetic Nanostructures with Soft X-rays

Y.U. Idzerda, Montana State University

Because of its elemental specificity and significant probing depth, x-ray spectroscopy, imaging, and scattering are unique tools for understanding buried nanostructures. With the addition of magnetic contrast from polarization control of the incident light, synchrotron-based soft x-ray characterization has already proved to be a powerful tool in understanding outstanding problems in the field of magnetism and magnetic nanostructures. Soft x-ray absorption spectroscopy can be, and has been used to follow the evolution of the electronic structure of small particles from a few atoms to large nanoclusters; to elucidate the effect on the electronic and magnetic structure of nanoparticle coatings and nanoparticle self-assembly; and to investigate electronic and magnetic response to the unique stresses associated with nanostructure formation. X-ray resonant scattering and imaging (with the magnetic counterparts, x-ray resonant magnetic scattering, and imaging with x-ray polarization selection) have complemented the electronic probes to characterize structure and assembly. Because soft x-rays probe the appropriate nanometer length scale, they are ideal for determining the overall size and shape of nanostructured elements and for determining inter-element assembly and interactions. These techniques have extended our understanding in the technologically important areas of exchange bias, magnetic nanoparticle interactions, and for characterizing the new-classes nanostructured magnetic semiconductors and half-metals. The simultaneous electronic, magnetic and structural characterization of buried nanostructures is a demonstrated and unique capability of soft x-ray absorption, imaging, and scattering.

With the continued improvement of high brightness, stable, polarization selectable x-ray sources, future developments in nanoscale characterization can benefit from advances in end-station capabilities and detector capacity. X-ray absorption can always be incorporated as a component of x-ray scattering or imaging to allow for simultaneous electronic and structural studies. Of particular importance are the new advances in coherent light scattering and lens-less imaging that have tremendous potential for understanding interacting nanostructures. Complimentary studies of both the average behavior of many nanostructures and the specific behavior of a single nanostructure are needed. More difficult is the incorporation of high time resolution for dynamic studies or *in situ* nanoparticle synthesis and assembly to characterize these processes. Only by understanding the synthesis and formation processes can substantial control be afforded.

X-rays and Neutrons for Directed and Self-Assembly

Eric W. Kaler, University of Delaware

Self-assembly driven by thermodynamics and directed self-assembly guided by external fields,offer two important ways to form heterogeneous nanoscale structures. When the structures have characteristic length scales on the order of 1 to 100 nanometers they are ideally examined by small-angle scattering methods, and both x-rays and neutrons have advantages. Dynamic processes can also be probed by neutron spin echo methods. A range of examples of the power of SAS arise from the study of surfactant self-assembly into micelles, vesicles, and microemulsions. The characterization methods for these assemblies, and the ability of small-angle neutron scattering in particular to provide unique information, are highlighted here.

Of particular utility is that polymerization reactions can be carried out in microstructured fluids such as microemulsions and vesicular solutions to yield novel polymer molecules and nanostructures. (Microemulsions are equilibrium phases that contain immiscible liquids such as oil and water stabilized by a surfactant film). We have carried out polymerization of several monomers in oil-in-water microemulsions and have produced very stable monodisperse lattices with particle sizes as small as 10 nm. Fast polymerization rates, high conversions and ultra-high molecular weight polymers are achieved with both oil-soluble and water-soluble initiators. A theory of the process will be sketched along with confirmatory novel SANS experiments. Further analysis isolates the effects of monomer water solubility, glass transition temperatures, and termination processes on the polymerization pathways. A fairly complete description of the process is in hand.

Closed spherical polymer shells can be synthesized via polymerization of monomers taken up in closed surfactant bilayers called vesicles. Typical vesicle dispersions are formed by mechanically disrupting a lamellar phase, but vesicles form spontaneously in mixtures of cationic and anionic surfactant. Proper use of surfactant mixtures avoids syntheses of specialized surfactant molecules, and indeed the electrostatic interactions of anionic and cationic surfactants makes available a rich variety of microstructures. The unilamellar vesicles that form spontaneously can be used as templates or molds for polymerization reactions, and the resulting products are characterized by cryo-TEM and scattering experiments.

Finally, new examples of instrumentation for SAS measurements will be discussed.

Scattering Techniques for the Characterization of Silicon Based NanoMaterials

Ginam Kim and Christopher McMillan, Dow Corning Corporation

X-ray and neutron scattering has become a necessary characterization technique not only for inner structural study, but also for the study of surfaces and interfaces of silicone base nanomaterials. For the development of novel nano materials in Dow Corning, the microstructure study related to their physical and chemical properties is fundamental. For this, scattering techniques have been effectively used for the study of fine scale phenomena in materials. In the study of nano,porous, thin films for dielectric (low-k) applications, the combined methods of x-ray reflectivity and SANS at NIST provided the information on film thickness, average mass density, density depth profile, wall density, porosity, average pore size, pore spacing, pore connectivity, and atomic composition. The results indicated that lower dielectric constant films have larger porosities and average pore sizes but lower wall densities. Scattering techniques were also used for the characterization of silicone modified dendritic polymers. Small angle neutron scattering measured the radius of gyration of dendrimers which is an average spatial distribution of all the units and the results indicated that the dendrimers are spherical. For the study of polymer nanocomposite, such as PS-PDMS block copolymers, small angle x-ray scattering monitored the phase segregation behavior of two different block components in the block copolymer under various thermodynamic conditions.

The well-ordered pattern in the block copolymers can be varied via the chain length, the weight ratio of block components, and the processing conditions. In Dow Corning, current research fields such as carbon nanocomposites with silicone polymers, photoluminescent nanoparticles, the development of thin film barrier material and nano vesicles also require scattering techniques to understand and control the structural behavior in order to obtain desirable physical properties. Demand for establishing expertise and developing scattering techniques for advanced materials research within Dow Corning is increasing and drives our interest.

Small is Different: Emergent Behavior in the Nanoscale

Uzi Landman, Georgia Institute of Technology

Investigations of physical systems of small sizes and reduced dimensionalities, exhibiting discrete quantized energy level spectra and specific structures and morphologies, open avenues for systematic explorations of the physical factors and unifying principles that underlie the transition from the atomic and molecular domain to the condensed phase regime. Such behavior, where the properties do not scale with the reduced physical size, but rather where *small is different* in an essential way that can not be deduced through extrapolation from knowledge of bulk behavior, is *emergent* in nature. Often, the *new and different* behavior at the nanoscale can be traced to the circumstance where one (or more) of the physical dimensions of the material aggregate approaches a length scale characteristic to a physical phenomenon (with different phenomena being characterized by different length scales).

Gaining insights into the nature of physical and chemical systems of highly reduced sizes, and developing experimental and theoretical methodologies aimed at probing, manipulating, and controlling them on the atomic and molecular level, are among the major challenges of current basic interdisciplinary research. Computationally-based theoretical modeling and simulations play an increasingly important role in modern condensed matter physics, chemistry, materials science, and biology. In particular, such studies, that may be called *"computational microscopies,"* allow explorations of complex phenomena with refined resolution in space and time [1].

The use of *atomistic simulations as tools of discovery* will be discussed and demonstrated through studies of: liquid nanojets and lubricated nanojunctions, hydrogen welding and switching in gold nanowires, the surprising nanocatalytic activity of small gold aggregates, post-ionization counterion-assisted hole transport in DNA and the mechanism of the reaction of ionized DNA with water that may cause mutagenesis and disease.

References

1. U. Landman, Materials by numbers: Computations as tools of discovery, perspective article in *Proc. Nat. Acad. Sci. (USA)* **102**, 6671 (2005). doi:10.1073/pnas.0408038102

Biological Applications and Opportunities for Nanoscience

Carolyn A. Larabell[1,2,*]

[1]University of California, San Francisco

[2]Lawrence Berkeley National Laboratory

I will present two examples of biological applications made possible by advances in the nanosciences. First, I will describe the ability to obtain 3-D reconstructions of whole cells in their native environment. Clearly the development of modern synchrotrons was critical to the development of this technology, but equally important was the significant progress in the develoment of zone plate optics. These diffractive lenses have enabled collection of biological images at better than 50 nm resolution, and continued improvements are on the horizon since these optics are now capable of achieving 15 nm resolution on test specimens. More important, we are not yet at the fundamental limits since we are using a 2.4nm wavelength source. Continued nanofabrication developments are required to further enhance the resolution capabilities.

Second, I will describe the use of semi-conductor nanocrystals (quantum dots, or QDs) to examine cell behavior associated with the invasive potential of cancer cells. Tumor cells engulf the fluorescent nanocrystals as they crawl and leave behind a fluorescent-free trail. The relative area of this trail can be directly related to degree of tumor invasiveness. We also used QDs to examine the interactions between breast tumor cells and human mammary acini (clusters of polarized epithelial cells that closely resemble functional breast tissue). These studies of 3-D tissue cultures revealed that polarized cells ward off invasion of tumor cells by a mechanism that results in apoptosis of the tumor cells. This behavior is not observed in cells grown in typical 2-D culture systems. Use of QDs enabled individual cells to be tracked over the extended time periods required for these studies.

Neutron Studies of Adsorption on Novel Nanometer Materials

J. Z. Larese, University of Tennessee and Oak Ridge National Laboratory

Neutron scattering techniques are particularly well suited for exploring the structure and dynamics of molecules adsorbed to or entrained within materials having a high surface-to-volume ratio. Using a combination of synthesis, thermodynamic, and elastic and inelastic neutron and computer simulation techniques we have investigated the adsorption properties of monolayer and multilayer molecular films on a variety of carbon-based and metal oxide nanometer-sized materials. Many of these experiments can be considered as a prelude for understanding surface mediated chemical reactions. Current efforts are aimed at understanding the structure and dynamics of nanoscale catalysts, the catalytic supports and reactant-catalyst interactions using model catalysts, and the metal oxide supports decorated with nanometer sized metal and bimetallic clusters. Studies of translational, rotational, and vibrational motion combined with structural measurements yield microscopic information about molecule-molecule and molecule-surface interactions, barriers to rotation, and reaction intermediate species. This microscopic information can be combined with electronic, chemical, and thermodynamic data to develop realistic models of the potential energy surface and reaction mechanisms. *In situ* studies under reactive and non-reactive conditions are needed to determine the dynamics of reactions and transformation of adsorbed species on heterogeneous catalysts and to provide fundamental insights into catalytic mechanisms, reaction intermediates, and catalyst deactivation/poisoning processes. Instrumentation that enables these *in situ* studies to be performed and is compatible with the neutron scattering environment must also be developed. Many of these studies have been performed in Europe (ISIS and the ILL) because current US neutron fluxes are limited and instrumentation is not yet available. VISION, a neutron vibrational spectrometer with simultaneous diffraction capabilities is currently being developed for the Spallation Neutron Source and will provide significant opportunities to investigate a wide range of nanometer scale materials including sorbents, catalysts, and catalytic supports.

Neutron Scattering Probes of Phase Separation and Interface Magnetism in Magnetic Oxides and Metallic Heterostructures

Chris Leighton[1], M. Lund[1], J. Wu[1], S. Park[2], M. Fitzsimmons[2], J. Lynn[3], C. Glinka[3] and J. Mitchell[4]

[1]University of Minnesota

[2]Los Alamos National Laboratory

[3]National Institute of Standards and Technology

[4]Argonne National Laboratory

I will provide a couple of examples of the use of current polarized neutron reflectometry (PNR) and small-angle neutron scattering techniques in the study of important problems in nanomagnetism. Using PNR we have probed the depth-dependent chemical and magnetic scattering density profile at antiferromagnet–ferromagnet interfaces to elucidate the physics behind the exchange bias phenomenon. This exchange bias effect is of fundamental interest in addition to being used in technological applications in the magnetic recording industry. Surprisingly, we observe a temperature-dependent *magnetic* interface location, which is ascribed to a strongly temperature-dependent competition between antiferromagnetic and ferromagnetic interactions in the interdiffused region near the interface. This example highlights the use of PNR to examine the general issue of the relationship between chemical and magnetic interface morphologies.

In the second example we have used SANS to probe the magnetoelectronic phase separation that occurs in doped perovskite cobaltites. This phase separation is intrinsic (i.e., it occurs in the absence of chemical segregation), is common to numerous transition metal oxides, and plays a key role in their most intriguing properties, such as colossal magnetoresistance and high temperature superconductivity. Small angle neutron scattering reveals the formation of close-packed nanoscopic ferromagnetic clusters in a non-ferromagnetic matrix, allowing for the observation of giant magnetoresistance-type phenomena in a system that has no chemical interfaces. This opens up the possibility of using this phase separation to fabricate “interface-less” nanostructures with useful properties.

Finally. I will discuss some areas, such as inelastic scattering from thin films and nanostructures and critical improvements in sample environment, which, if realized, would allow for great advances in many nanomagnetism problems. In particular, I will emphasize the potential benefits that would be provided by the ability to routinely probe spin wave excitations in thin film heterostructures, and magnetic Bragg reflections in relatively thin films.

Nanomagnetism: Relevance, Issues, and Tools

Laura H. Lewis, Brookhaven National Laboratory

Nanostructured magnetic materials form the basis of a variety of functional devices that support National strategic missions. These include ultra-strong, light-weight magnetic components; highly efficient electrical transformers and vibrational energy harvesting devices to foster energy independence; new medical protocols for advanced health care; and new spintronic technologies that streamline communications and stimulate the economy. The phenomenon of magnetism itself is determined by the local electronic bonding environment and is hence inherently a nanoscale issue. Very subtle aspects of the local structure (e.g., 1-, 2- or 3-D defects, antisite occupancies, variable compositional and roughness profiles and strain) can alter the magnetic exchange length and create a dramatic change in the macroscopic technical magnetic properties such as remanence and coercivity. Such information is largely missing from most nanostructured magnetic materials studies.

Harnessing the potential of nanostructured magnetic materials requires atomic-level, element-specific probes that simultaneously monitor the magnetic response and the lattice structure with variable temperature capability in applied magnetic, electric, and strain fields. In particular, correlation between the magnetism and the structure at an interphase interface is of specific interest, especially for the so-called "buried interfaces" inherent to nanostructured magnetic systems. It is essential to capture the magnetism and structure of interfaces located far from the free surfaces. While these interfaces are well defined in thin film multilayer geometries, the more challenging interfacial regions of granular films and nanocrystalline bulk materials also warrant attention.

As the key element to this challenge is the ability to non-destructively probe matter at specified depths, there are opportunities for both synchrotron and neutron radiation. All techniques may be applied, including scattering, imaging and spectroscopy. The synchrotron radiation feature of element specificity is very important. Improvements in depth resolution and beam size are desirable, as are features such as *in situ* application of temperature and fields (magnetic, electric, and strain). Real-time coupled structural and magnetic imaging of interfaces under *in situ* annealing conditions would be an exciting way to elucidate subtle structure–magnetism connections in magnetic nanomaterials.

Small Angle X-ray Scattering/Diffraction of Supramolecular Assemblies

Youli Li and Cyrus Safinya, University of California, Santa Barbara

One of the areas in which x-ray and neutron techniques can made a big impact is in studying the structure and interaction of supramolecular assemblies of macromolecules (e.g., polymers, proteins and nucleic acids) as well as nanoparticles self-assembled in solution or on surfaces. The formation of these hierarchical structures with length scales spanning a few nanometers to thousands of nanometers is driven by a variety of interactions, including specific (e.g., chemical bonding) or non-specific (e.g., electrostatic and hydration forces, etc.) ones. Understanding the nanoscale structure and interaction, and ultimately achieving control of the self-assembly process, has far-reaching scientific and technological implications. Nature provides us with ample examples of self-assembly in work; for example, a large number of sub-cellular structures (e.g., cytoskeleton) are formed and controlled through this process. The multitude of structural morphologies exhibited in nature has lent much inspiration to producing man-made nanostructured materials for a broad range of applications including drug and gene delivery agents, nanoporous networks, miniaturized biosensors, etc.

Applying x-ray and neutron techniques to study self-assembly presents some unique challenges. One common characteristic of the self-assembled structures is the low degree of ordering in the material, which weakens the scattering signal. Consequently, the data quality improves tremendously by using high brilliance sources. In addition, the low scattering angles associated with the large length scale (1 nm to 100 nm) of the structure require special data collection as well as analysis methods. Small angle x-ray scattering and small angle x-ray diffraction (SAXD) are the most common tools used for investigating the structures of supramolecular assemblies.

To elucidate the complex structures of self-assembled materials generally requires the application of multiple structural tools. We have used SAXS and SAXD, in conjunction with real-space imaging techniques (optical and electron microscopy) to solve a number of unique structures of the lipid-biopolymer (e.g., DNA, RNA, actin, microtubules) complexes. The complementary information provided by imaging proved crucial to the construction of the structural model which would fit the scattering data. It would be extremely useful to build instruments which perform two of more types of measurements simultaneously on the same sample. For example, by combining an epi-fluorescence or confocal optical microscope with a cutting edge SAXS instrument it would enable the investigation of structural features at the nanoscale and microscale at the same time, which would dramatically enhance the capability of each technique by itself.

Another area in which a consorted effort could be directed is to develop software tools that can perform sophisticated analysis and modeling of scattering data from non-crystalline samples with an easy-to-use interface. The huge success of protein crystallography can be partially attributed to the development of such packages. However currently there is no generalized software tools available to model partially ordered (1-D and 2-D) or completely disordered systems, which characterize most self-assembled nanostructures. This limits the ability of nonexperts to derive maximum information from their data. The National Nanotechnology Initiative can play an important role in initiating and supporting these efforts.

Nanomaterials Science at the Advanced Photon Source

Gabrielle Long, Jörg Maser, George Srajer, Jin Wang, Barry Lai, Qun Shen, Argonne National Laboratory

X-ray tools for nanomaterials science enable the quantitative analysis of compositional, structural, chemical, magnetic, and dynamic properties at the interatomic, atomic, and molecular level over a wide range of time scales and including *in situ* capabilities. The Center for Nanoscale Materials (CNM), currently under construction in partnership with the Advanced Photon Source at sector 26, will be dedicated to the development and characterization of novel materials and devices at the nanoscale.

The CNM Hard x-ray Nanoprobe Facility will provide unique hard x-ray microscopy capabilities dedicated to the study of nanoscale materials and devices. The Nanoprobe will provide analytical capabilities at a spatial resolution of 30 nm, and provide fluorescence spectroscopy, diffraction imaging and microdiffraction and high-resolution transmission imaging.

In addition to the Nanoprobe instrument, the APS provides numerous complementary experimental facilities that serve the community of nanoscience researchers in the areas of interfacial structures, nanosystems, confinement, and self-assembly of hard materials, soft materials, and biomaterials, or nanofluidic phenomena. These facilities include several nanoprobes around the APS ring:

- X-ray-excited optical luminescence (XEOL) sensitive to structures < 10 nm
- soft-x-ray photoelectron emission spectroscopy (PEEM)
- 6 – 13 keV scanning fluorescence microscopy and micro/nanodiffraction (70 nm probe)
- 1 keV – 4 keV scanning transmission microscopy, scanning fluorescence microscopy, and coherent scattering (50 nm probe)

In addition to these imaging techniques, x-ray scattering provides another important approach to the study of nanoscale materials. Capabilities at the APS include:

- characterization of magnetic interfaces using magnetic reflectivity
- small-angle x-ray scattering and grazing incidence small-angle x-ray scattering for following, *in situ* and in real time, the formation of nanocrystal monolayers, nanoparticle arrays and the associated kinetics
- coherent diffraction, currently under development at the APS and sometimes called "lensless imaging," for imaging structures at the nanoscale
- diffraction under *in situ* growth, including MBE, MOCVD, and PLD
- x-ray photon correlated spectroscopy (XPCS)

Characterization of Functionalized Biomimetic Membranes

Mathias Lösche, Johns Hopkins University and CNBT consortium at the NIST Center for Neutron Research

A new neutron spectrometer–the *Advanced Neutron Diffractometer and Reflectometer (AND/R)*–has been recently commissioned by the *Cold Neutrons in Biology and Technology* (CNBT) research consortium, a U.S. university/government lab research partnership located at the NIST Center for Neutron Research. This new instrument is optimized to investigate specifically problems in membrane biology and biotechnology. These are mostly concerned with dynamic, structurally disordered systems. Thus, molecular dynamics simulations, solution scattering, and NMR are an integral part of the CNBT mission. Investigations in the first year of AND/R operation include studies of surface-grafted DNA, chain interdiffusion within polyelectrolyte multilayers, and high-resolution structures of hydrated lipid membranes. This contribution will focus on studies of surface-tethered membrane structures for the development of robust sensing applications.

The CNBT is funded by the NIH (1R01 RR14182), NIST, and the Regents of the University of California. The reported research is also funded by the NSF (NIRT 0304062).

Superlattice Crystals for Forefront Neutron Science

Doug Lowndes, Hans Christen, and Ho Nyung Lee, Oak Ridge National Laboratory

The outstanding challenge of 21st Century science that can be addressed by neutron scattering is the need to understand self-organizing behavior that first emerges on the nanoscale in chemically complex systems. Electronically highly correlated and structurally similar complex oxides epitomize this challenge, by exhibiting a rich variety of electrically conducting and insulating behavior, high-temperature superconductivity, magnetism, colossal magnetoresistance, and ferroelectricity. In the words of Birgenau and Kastner, these phenomena "present us with profound new problems that … represent deep and formidable challenges…", for which "…neutron scattering is an absolutely indispensable tool " [1]. However, the most revealing neutron scattering studies require single-crystal samples of significant size. Moreover, conventional crystal growth offers limited capacity to design novel samples for interesting experiments.

In contrast, new understanding and methods for pulsed laser deposition (PLD) recently enabled us to grow 1 μm thick oxide heterostructures with atomic-layer control and complete reproducibility of interfacial and surface quality over thousands of unit cells. These advances were demonstrated by carrying out the first experimental verification of theoretically predicted polarization enhancements in artificial PLD ferroelectric "superlattice crystals" grown from periodically repeated strontium titanate ($SrTiO_3$), barium titanate ($BaTiO_3$), and calcium titanate ($CaTiO_3$) building blocks [2]. Subsequent simulations and experience-based estimates show that PLD growth of crystalline heterostructures with sufficient mass for the full range of bulk-like neutron scattering measurements—reflectometry, diffraction, and inelastic scattering—now is feasible.

Consequently, there is now an outstanding opportunity and need to build a first-of-its-kind "superlattice crystal" growth facility to provide *thick* (up to 100 µm) epitaxial oxide heterostructures for forefront neutron scattering studies at the Spallation Neutron Source (SNS). This growth facility will permit neutron scattering to move beyond the limits currently imposed by conventional crystal growth. Novel properties are known often to result from the competition between the physical dimensions of nanostructures and the length scale(s) relevant to magnetism and other collective phenomena. Consequently, the *ability to control the dimensions of individual components within multilayered samples at the nanoscale* is *essential***.** Others also have pointed out recently that the *design* of novel samples should be *an integral part of the planning process* for a major new neutron scattering facility [3]. The benefits of developing a PLD-based epitaxial heterostructure growth facility will be to fully engage the international scientific community—theorists and experimentalists —in designing materials to create new phenomena, and to greatly enrich the data stream resulting from the national investment at the SNS.

References

1. R. J. Birgenau, M. A. Kastner, Frontier physics with correlated electrons, *Science* **288** (5465), 437 (2000). doi:10.1126/science.288.5465.437
2. Ho Nyung Lee, Hans M. Christen, Matthew F. Chisholm, Christopher M. Rouleau, Douglas H. Lowndes, Strong polarization enhancement in asymmetric three-component ferroelectric superlattices, *Nature* **433**, 395-399 (2005). doi:10.1038/nature03261
3. Paul Canfield, Ames National Laboratory, Abstract submitted to planning workshop on high magnetic fields for x-ray and neutron scattering, Tallahassee, Florida, May 10-13, 2005.

3-D Coherent Diffraction Microscopy and Its Applications in Nanoscience

Jianwei Miao, University of California, Los Angeles

Visualizing the arrangement of atoms has played a crucial role in the rapid progress of nanoscience and technology. There are already a few ways of imaging atomic structures, but each has its limitations. Scanning probe microscopes are limited to imaging atomic structures at the surface. Transmission electron microscopes can resolve atoms, but only for samples thinner than ~ 30 nm. Crystallography can reveal the globally averaged 3-D atomic structures based on the diffraction phenomenon, but requires crystals. These limitations can in principle be overcome by coherent diffraction microscopy based upon coherent x-ray scattering in combination with the direct phase recovery method called oversampling. Coherent diffraction microscopy has been successfully applied to 2-D and 3-D imaging of nanoscale materials and biological systems. A highest spatial resolution of 7 nm has been achieved, while the ultimate resolution is only limited by the x-ray wavelengths. By using third-generation synchrotron radiation sources, better-designed instruments, and more robust image reconstruction algorithms, we expect to improve the spatial resolution to the 1 nm level within the next few years.

Meanwhile, we will also pursue its applications in materials and nanoscience. We will focus on 3-D imaging of porous silica particles, gallium nitride (GaN) semiconductors, quantum dots and mineralized bone. The ability to image the internal pore structures in three dimensions, (e.g., 3-D morphology of GaN and its alloys in nanocrystal form, and 3-D internal structures of quantum dots), coupled with computational methods such as molecular dynamics and *ab initio* calculations, will profoundly expand our understanding of the critical structural and morphological features required to make superior catalysts, adsorbents, electrodes, or semiconductors. Understanding the mineral component of bone such as the size, shape, and arrangement of the calcium apatite crystals in a collagen matrix will be of fundamental importance in biology and medicine.

In the long run, with the prospects of brighter x-ray sources such as the Linac Coherent Light Source and pixel array detectors of higher quantum efficiency and a higher dynamic range, coherent diffraction microscopy can potentially be used to determine the 3-D structures of single particles down to the atomic level.

References

1. I. K. Robinson, J. Miao, *MRS Bulletin* **29**, 177-181 (2004).
2. J. Miao, H. N. Chapman, J. Kirz, D. Sayre, K. O. Hodgson, Taking x-ray diffraction to the limit: macromolecular structures from femtosecond x-ray pulses and diffraction microscopy of cells with synchrotron radiation, *Annu. Rev. Biophys. Biomol. Struct.* **33**, 157-176 (2004). doi:10.1146/annurev.biophys.33.110502.140405
3. G. J. Williams, M. A. Pfeifer, I. A. Vartanyants, and I. K. Robinson, three-dimensional imaging of microstructure in Au nanocrystals, *Phys. Rev. Lett.* **90**, 175501 (2003). doi:10.1103/PhysRevLett.90.175501
4. J. Miao, T. Ishikawa, B. Johnson, E. H. Anderson, B. Lai, and K. O. Hodgson, High resolution 3D x-ray diffraction microscopy, *Phys. Rev. Lett*. **89**, 088303 (2002). doi:10.1103/PhysRevLett.89.088303

Improvements to Existing Facilities for the Study of Nanoscale Materials

Paul F. Miceli, University of Missouri

Quantum size effects in nanoscale materials with reduced dimensions can have a profound influence on the properties of a material and on the way materials assemble and grow. A more significant effect, however, is the role played by surfaces, interfaces, and internal defects, which can dominate the energetics of these small systems. Therefore, in order to ultimately harness potential applications of nanoscale materials, we will need to understand their structure. Surface x-ray scattering has a truly unique role to play here because of its ability to obtain both surface and subsurface structure over a range of length scales. Our studies of metals have amply demonstrated the importance of looking at subsurface structure in relation to the surface.

The small bright beams provided by third generation synchrotron radiation sources are well suited for these studies. Two significant improvements would better utilize what we already have.

1) As x-ray sources and optics have developed, a similar development of detectors has not kept pace. There is a need for faster multielement detectors for real-time measurements; detectors with significantly larger dynamic range of count rate; and for multielement energy sensitive detectors.

2) There is a need to expand the available beam time for *in situ* studies, which are essential for understanding nanoscale phenomena. *In situ* studies in general and *in situ* surface science studies in particular are time consuming measurements. This fact needs to be recognized when designing

beam lines and allocating time. A second important facet of this problem concerns student training. Since surface scattering experiments require a “sophisticated user,” student training needs to allow the time for students to make some mistakes and work independently. It is a crucial consideration for producing the next generation of scientists who will develop future infrastructure.

Regarding neutron sources, existing smaller satellite reactors can play a significant supporting role for national facilities. Unlike laboratory x-ray sources which are many orders of magnitude weaker than synchrotron sources, satellite reactors are only a factor of 2 to 10 weaker than national facilities. Thus, satellite reactors can provide much needed training, concept and instrument development, as well as supporting research for the national facilities. This model has been successfully employed in Europe for decades.

Magnetic Excitations in Dimensionally Restricted Systems

Stephen Nagler, Oak Ridge National Laboratory

With the advent of next generation neutron sources inelastic scattering measurements will be possible on smaller sample masses and with higher resolution than has been achievable to date. Characterization of the excitations in systems with nanoscale dimensional restriction should become possible. Examples include thin films and multilayers, arrays of magnetic nanowires, assemblies of magnetic nanoparticles or quantum dots, magnetic molecules, and magnetically dilute systems.

Marrying Reaction Chemistry to Surfaces

Colin Nuckolls, Columbia University

This presentation will explore methods to direct the assembly of molecular wires on metal and metal oxide surfaces and to measure their electrical properties in nanoscale test structures. Attachment of aromatic molecules to oxide surfaces using multivalent interactions provides high coverage monolayers. Synchrotron reflectivity on these monolayers reveals that they are as tightly packed as molecules in bulk crystalline state. These tightly packed monolayers spontaneously assemble to form monolayer field effect transistors.

A parallel effort is developing the chemistry to grow wires from metal surfaces. The presentation will explore new monolayers that form on some metal surfaces reacted with carbenes. These monolayers are exceedingly stable and are able to initiate olefin metathesis. This interfacial chemistry provides a method to both structurally and electrically contact molecules on metal surfaces.

Patterned Nanoscale Materials

Teri W. Odom, Northwestern University

This talk will focus on how patterning and synthesis at the nanometer-scale enable unique ways to study a broad range of scientific queries. Our research uses developments in nanopatterning to address important problems in chemistry, materials, and photonics. This combination has significant promise for the discovery of new fundamental principles in physical chemistry and the advancement of sensitive and powerful analytical techniques. Using a variety of unconventional patterning methods, we have generated nanostructured surfaces with three-dimensional features at nanometer length scales and over cm^2-areas in a single step; moreover, these patterns exhibit hierarchical order and selective chemical functionality from which to build or assemble new types of mesoscale (100 to 1000 nm) structures. One outstanding issue is the characterization of nanostructures on surfaces.

X-ray scattering at small angles can help solve the crystalline structure, the size distribution and orientation, and the interface between the surface and the nanoscale materials. One way that the current resources can be applied to nanoscience problems is to construct a simple but informative site that lists common challenges of nanoscale characterization—and then how x-ray/neutron techniques can solve them. Individual principal investigators could then contact the appropriate scientists to set up collaborations and analyses.

Functional Bio-Nano Molecular Materials: Is there Something to Learn from Mother Nature?

P. Pincus, University of California, Santa Barbara

Nature synthesizes functional materials in an integrated and highly controlled manner. The study of this integrated system is the realm of the developing field of *systems biology*. Biology celebrates diversity but at the molecular/cellular levels, a few motifs are seen repeatedly. We provide some examples in the context of functional materials. These include hierarchical assembly, motor-driven synthesis, programmed assembly, and functional materials. A challenge for the neutron and x-ray communities is to provide tools for the characterization of hierarchical systems at both the static and slow dynamical levels.

Challenges for X-ray Characterization of Nanoscale Soft Matter Assemblies

Ron Pindak, Brookhaven National Laboratory

The soft matter systems that are being studied at the nanoscale are often hybrid assemblies, for example, nanoparticles in a polymer matrix or inorganic nanocrystals decorating organic fibrils. Such hybrid systems incorporate ordering from nanometer to micrometer length scales with the local atomic structure and associated functionality being as important as the long-range correlations. The systems are often radiation and environmentally sensitive; when fabricated into devices they contain a range of different types of buried interfaces, are usually solution-processed, and their assembly is often directed by mechanical constraints, chemical templates, or external fields. The x-ray characterization of the evolving structure of these hybrid systems, under processing conditions, presents considerable challenges for current synchrotron x-ray facilities.

The current trend at synchrotron facilities is to instrument and staff beamlines optimized for a specific x-ray technique. This specialization offers advantages in terms of rapid access to standardized set-ups as well as access to instrumentation that is fine-tuned for specific techniques. These optimized beamlines, especially x-ray nanoprobe and SAXS-GISAXS beamlines with *in situ* processing chambers and complementary probes, will address most of the characterization needs for soft matter nanoscience assemblies. Nonetheless, we propose that there will continue to be a need for "general-purpose' beamlines to provide the flexibility for researchers to develop new approaches to sample characterization. In this presentation, we will describe two efforts to develop new approaches for soft matter characterization utilizing "general-purpose" undulator beamlines. One project involved the study of 100 μm x 100 μm patterned alignment areas of layered liquid crystals created using AFM-scribed polymer alignment coatings while the second project involved an analysis of crystal truncation rods to determine model-free electron density maps of semiconducting organic thin film interfaces. Future refinements of these techniques will be described along with the features of the "general-purpose" diffraction beamlines which made their initial implementation feasible.

Advanced Instrumentation for Neutron Scattering Studies of Nanoscale Materials

Roger Pynn,Los Alamos National Laboratory

Fundamental properties of the neutron's interaction with matter make neutron scattering a tool that is especially well suited to characterizing the structure and low-energy dynamics of both hydrogen-containing and magnetic materials. The technique has already contributed significantly to research on nanoscale materials of these types, such as complex fluids and magnetic multilayers. I will present some illustrative examples to show the range of information that has been obtained. To make neutron scattering even more useful for the characterization of nanoscale materials, several more or less serious impediments will need to be overcome through the development of a new generation of neutron scattering instrumentation and through the coupling of neutron instrumentation and high performance computer simulation. I will discuss in some detail one of the more serious impediments—the fact that neutron scattering is a signal-limited technique. One consequence of this is that it is difficult to study small or dilute samples, features that are quite common for nanoscale materials produced either by self-assembly or by deposition techniques. A second consequence arises because nanoscale materials display order on length scales that are typically between one and three orders of magnitude larger than the wavelengths of cold neutrons. Resolving such length scales with neutron diffraction generally demands tight collimation of the neutron beam, reducing the neutron count rates and limiting the statistical precision of the measured neutron intensity. I will discuss these limitations and suggest ways in which they might be overcome with a new generation of neutron scattering instrumentation.

Reinforcing Polymer Composites with Protein Functionalized Nanotubes

Marie-Louise Saboungi, CRMD-CNRS

We have developed fully integrated nanotube composite materials through the functionalization of multiwall carbon nanotubes (MWCNTs) by covalently attaching ferritin protein molecules onto their surface. The investigation of the thermo-mechanical behavior was performed by dynamic mechanical thermal analysis (DMTA). The results demonstrate a dramatic enhancement in the mechanical properties polyvinyl acetate (PVA) for example a 100-110% increase in the modulus with the addition of 1.5 wt% of ferritin-functionalized MWCNTs. Samples containing functionalized nanotubes show a stronger influence on glass transition temperature than composites containing the same amount of non-functionalized nanotubes.

High-resolution neutron scattering studies with back-scattering and/or spin echo techniques as the glass transition is approached from above would provide a microscopic picture of the macroscopic dynamics probed by the mechanical property measurements. In addition, inelastic neutron scattering could be used to confirm the covalent bonding between amino and carboxylic functionalities on the surface of ferritin functionalized nanotubes and the PVA matrix.

Probing Nanomagnetism with Neutrons and Advanced Simulations

Thomas C. Schulthess and Mark Hagen, Oak Ridge National Laboratory

In recent years there has been wide interest in the study of highly anisotropic magnetic nanoparticles. Besides basic science interests, there are important applications of these systems for future data storage and information processing technologies as well as permanent magnets. Significant progress has been made in the synthesis of mono-disperse assemblies of complex nanoparticles, such as iron-platinum (FePt), cobalt-platinum (CoPt), and various transition metal oxides. However, the understanding of their magnetic properties has been lagging behind, largely due to lack of adequate experimental probes. One of the urgent issues seems to be the understanding and control of the magnetic switching in nanoparticles. It appears that these processes are more complex than expected from simple models. But the involved length and time scales are outside the reach of conventional magnetization measurement techniques.

Here is where a systematically coordinated effort of polarized neutron scattering experiments and advanced theory and modeling can make significant contributions. Neutron scattering experiments are capable of probing magnetic structure as well as magnetic excitations at intraparticl and interparticle length scales. With advanced simulation techniques it is now possible to model from first principles the magnetic structure of nanoparticles and to reproduce the measured dynamic correlations functions of spin models. With a combined neutron characterization and modeling effort, it should be possible to fine tune spin models of nanoparticles. Parameters of these models can be gauged by comparison of the magnetic structure and excitations with first principles calculations and inelastic neutron scattering spectra, respectively. These models can subsequently be used to study magnetic switching and other properties, in order to help understand and guide more conventional magnetic characterization techniques.

The theoretical methods and software tools, as well as the neutron scattering techniques that are being developed in this effort, are not limited to magnetic nanoparticles. The coordinated effort of developing joint neutron scattering methods and simulation tools for magnetic nanostructures will therefore generate solutions to other characterization problems in nanoscience.

Neutron Refractive Optics and Peripheral Techniques and Their Applications

Hirohiko M. Shimizu, RIKEN

The small-angle neutron scattering (SANS) is a general tool to investigate the static structure in the mesoscopic region of about 1 nm to 100 nm. The neutron sensitivity to light elements enables us to observe the structure of soft-matters including polymers and proteins. Radiation damage to samples can be suppressed since the neutron does not have the electric charge and its kinetic energy is sufficiently low to avoid direct destruction of chemical bandings, which is due to the neutron mass comparable with atomic mass.

The focusing of cold neutron beam using refractive optics has been applied to extend the minimum value of accessible q-region (q_{min}) of spectrometers for small-angle neutron scattering at the Japan Atomic Energy Research Institute. The refractive optical devices were sextupole magnetic lenses and compound refractive lenses. The q_{min} was decreased from 10^{-2} nm^{-1} to 10^{-3} nm^{-1} by employing a scintillator-based neutron-imaging detector on the focal plane together with the focusing lens. If we extend the q_{min} by increasing neutron source intensity without the focusing lens, we need much more intense neutron source by two orders of magnitude. In other words, the “neutron utilization efficacy” was enhanced by two orders of magnitude.

The improved sensitivity introduces the SANS capability to observe long-term change in dilute soft-matter samples. The magnetic lens delivers a spin-polarized neutron beam, which enables to study magnetisms of nanoparticles. It also introduces possibilities to decompose the coherent and incoherent scattering components from hydrogen nuclei. A spin contrast variation would be possible by developing techniques to dynamically polarize protons in samples.

The polarizing power of magnetic lenses is calculable from the geometry of device arrangement. The polarization loss is expected to be negligible since there is no material on the beam path. Thus, we can expect an extremely high purity of neutron spin polarization together with well-defined beam distribution both in space and beam divergence. It can be applied to improve the performance of neutron spin echo techniques both in its maximum value of the Fourier time and q_{min}. It will contribute to observation of slow dynamics at nanoscale in soft materials.

Some Possible Challenges for Modeling Soft X-ray Spectra on the Nanoscale

Eric L. Shirley, NIST

Soft x-ray spectroscopic techniques can help characterize many properties relevant on the nanoscale. These properties include: chemical element identification, structure (in the sense of local atomic geometry), vibration properties, oxidation states of transition-metal ions, effects of ligands, and so forth. As an example, one may consider the detailed Fe 2p absorption spectrum of an iron ion surrounded by a cage of ligand oxygens and embedded in a large molecule. The local atomic geometric and iron oxidation state can be inferred in part from the multiplet structure of the Fe 2p edge. Charge-transfer excitations and other satellite features in the spectrum might provide further insight into the interactions between the iron ion, its nearest neighbors, and perhaps other surroundings. Ultimately, if theoretical treatments can describe spectra with great detail, high energy resolution could be increasingly valuable.

To perform modeling to support and interpret experiments, it is necessary to amplify current methods that are commonly used. There are several areas for potential improvement. Often, nanoscale phenomena occur at certain sites in artificial structures or large molecules. The "relevant volume" for some nanoscale phenomena of a physical system can be small compared to the total system, and yet large compared to typical unit cells of many crystalline solids. This entails large-scale computation to model physical systems, but hopefully with attention focused mostly on the relevant volume. In order to address this, one needs to consider how to efficiently yet accurately "embed" the relevant volume in a larger system, allowing for "communication" with the surroundings along the lines of dielectric screening, electron transfer, etc., subject to sufficiently realistic "boundary conditions." In particular, the ability to compute polarization and screening effects of electron–electron interactions in real space would be helpful, if the one-electron density matrix allows this.

In the previous example, there is also still room for improving the describing of even just the iron atoms and its ligands. It is difficult to solve the essentially configuration-interaction problem necessary to obtain a complete spectrum, and it is also difficult to know how to "truncate" one's physical system in real space, in order to account for the placement of the iron ion and its ligand within a larger system, without worsening results through artificially imposed boundary conditions or attempting to describe the quantum mechanics of an unnecessarily large physical system.

Synergism of Neutron Scattering and Molecular Simulations in Understanding Dynamics and Structure of Polymer-Based Nanomaterials

Grant Smith, University of Utah

Neutron scattering is one of the most important probes of structural and dynamical properties of polymers on the nanometer length scale. The power and utility of neutron scattering as applied to polymers is greatly enhanced when utilized in coordination with molecular dynamics simulation studies of the same material. The synergism between neutron scattering and molecular simulations is potentially even greater for polymer-based nanocomposites and self-associating nanomaterials. The potential for coordinated neutron scattering and molecular simulation studies to provide unique insight into the nanoscale structural and dynamical behavior of polymer-based nanomaterials as well as examples of synergism between neutron scattering and molecular simulations in studies of polymers and polymer nanocomposites will be presented.

Structural Studies of Confined Soft Matter — Surfaces and Interfaces

Gregory S. Smith, Oak Ridge National Laboratory

This area is wide ranging in both the materials studied and the methods of confinement. The materials include biomaterials (e.g., lipids and proteins), biomimetic materials, polymers, surfactants, liquid crystals, and small molecule liquids. Specifically, we are searching for novel materials properties and structures as macromolecules are confined in 2-D space. Two-dimensional confinement can be achieved in Langmuir monolayers (liquid-air interface), in solid-supported membranes or thin films (solid-liquid or solid-air interface), or by compressing thin films between parallel solid surfaces (solid-solid interface). In addition, controlled synthesis of nanomaterials and nanofabrication strategies provide an interface to biosystems on a nanoscale and allows one to probe, modify, or mimic live cell, cell components, or molecular structures, forming an emergent field of nanoenabled biology or simply nanobio. Creation of such nanoscale architectures is going to enable new strategies for probing biosystems with neutrons.

At the molecular level, our recent neutron reflectivity experiments have been very successful in providing detailed density distribution profiles of adsorbed diblock polymers confined between two substrates under good solvent conditions as a function of confinement. We are continuing to investigate polyelectrolyte brushes and extend these studies to include the ability to shear the polymer brushes. Combined with state-of-the-art techniques in polymerization and selective deuteration, we are building controlled model architectures to elucidate the structure of these complex systems at interfaces under confinement and applied shear stress. Futher development of neutron and x-ray scattering techniques such as grazing incidence diffraction may yield even more in-plane detailed structural information.

One way we can increase the chances of success of neutron and x-ray studies of these materials will be to develop the sample environment equipment needed in the labs and for neutron scattering experiments specific to these special materials. For example, we will continue the development of the confinement/shear cell and extend it to the study of lipid membranes. With the advent of the SNS, we can use smaller samples and get the smaller confinement gaps needed to study these systems which have intermembrane separations of approximately 5 nanometers. Similarly, continued development of new ways to modify the carbon nanofibers with various specificity will enable us to control the interactions between substrates and supported membranes.

Mesoscale Inhomogeneity in Colossal Magnetoresistive Manganites

Yeong-Ah Soh, Dartmouth College

Manganites display a complex phase diagram, with various types of spin and charge ordering as its ground state. More interestingly, the various phases of the manganites can coexist in the same sample, leading to an inhomogeneity in the physical properties ranging from the mesoscale down to the nanoscale. This inhomogeneity is considered to be important in explaining the large colossal magnetoresistance exhibited in this class of materials. Focused x-rays are ideal for addressing the inhomogeneous phases in manganites. I will discuss how the inhomogeneity in the magnetic ordering temperature and wavelength of charge density waves can be addressed using x-ray microdiffraction, and the insight that we gain about the origin of the inhomogeneity.

Heterogeneous Catalysis: Nanoscale Meets the Atomic Scale

Peter C. Stair, Northwestern University and Argonne National Laboratory

There is abundant evidence that the activity and selectivity of heterogeneous catalysts are controlled by a combination of properties at both the nanoscale and the atomic scale. It is now within the realm of possibility to synthesize catalytic nanoscale particles, supported on a solid surface, with control of both their composition and topology at the atomic level. The characterization of such materials, particularly the measurements required to prove the successful synthesis of a specific composition and structure, will require x-ray and neutron measurements that can penetrate both the gas or liquid environment of the catalyst and the catalyst material itself. These measurements will not only need to provide average composition and structural information, but provide cluster-by-cluster information. During my 5-minute presentation, I will provide some specific examples from my own interests.

In Situ X-ray Studies of Nanostructure Creation

G. B. Stephenson, Argonne National Laboratory

Some of the greatest challenges in nanostructure creation are associated with understanding and optimization of synthesis and patterning processes for novel materials (e.g., complex oxides, bio-inorganic composites, etc.). Many of these processes are difficult to probe at the atomic scale by traditional electron imaging or spectroscopy, including vapor-phase processes such as chemical vapor deposition, atomic layer deposition, and reactive ion etching, as well as aqueous solution growth and etching. X-ray scattering, spectroscopy, and imaging are ideally suited to provide the first *in situ* observations of the atomic-scale mechanisms of these processes.

This is a very exciting time for progress in x-ray capabilities. Now that extremely high brilliance sources are available or under construction, large payoffs can be anticipated from developments in optics, detectors, and specialized instruments such as *in situ* analysis facilities. In particular, breakthroughs in x-ray focusing optics indicate paths to achieve sub-10-nm resolution, which will provide powerful new imaging capabilities for nanostructures.

X-ray Studies of the Nanoworld — Motivation, Concepts, and Applications

Joachim Stöhr, Stanford Synchrotron Radiation Laboratory

In an era where many powerful techniques can provide images of the nanoworld, I will start my talk by addressing the unique capabilities of synchrotron radiation and synchrotron radiation techniques for the study of nanomaterials. The *short wavelength* allows resolving, seeing, and studying individual nanoobjects. The *tunable photon energy* provides access to resonance effects that are elemental- and chemical-state specific and exhibit large cross sections. The latter in combination with the *high photon beam brightness* provides sensitivity to a small number of atoms. Finally, the x-ray *polarization* allows the separation of charge and spin phenomena. The interaction of selected nanoobjects with the incident x-ray beam can be studied by a variety of experimental techniques that give electronic, magnetic, and structural information. I will present several examples where x-rays have provided unique information on nanostructures that cannot be obtained by any other technique. Finally, I will address the important correlation between space and time phenomena – the smaller the faster. I will emphasize that technological advances require exploration of both the ultra-small and ultra-fast. This exploration is the real strength of x-rays and the basis for revolutionary developments in the future.

Probing Magnetic Nanostructures by Polarized Neutron Scattering

S.G.E. te Velthuis, Argonne National Laboratory

Surfaces and interfaces greatly impact the characteristics of nanoscale materials. Therefore, in order to understand the physical properties, detailed characterization is essential. In the case of (magnetic) thin films and heterostructures with nanoscale thicknesses, (polarized) neutron reflectometry (PNR) has for many years been an excellent tool for probing (magnetic) interface structure. Polarized neutron reflectometry provides the depth dependent magnitude as well as the orientation of the magnetization, along with the structural parameters of a thin film.

Polarized neutron reflectometry studies of interface phenomena such as exchange bias and exchange coupling have led to a greater understanding in these areas. Materials nanostructured in three dimensions can be probed by small angle neutron scattering and by grazing incident scattering, in which the ensemble average of the properties is obtained. Again the depth sensitivity of surface scattering methods provides access to buried interfaces or layers that is hardly obtainable with other techniques. I will present various examples, illustrating the effectiveness of PNR, scattering at grazing incidence, and SANS in providing important information in magnetic nanoscale materials.

Neutrons, Pressure, and Nano Materials: Emerging Possibilities

Chris Tulk, Oak Ridge National Laboratory

A brief overview will be given of the extreme sample environment capabilities planned for the SNS. This will particularly include design and performance features of the Spallation Neutrons And Pressure diffractometer planned for completion in early 2008. In addition, examples of our recent experience with neutron microfocusing prototype devices will be discussed as it relates to augmenting high pressure neutron diffraction instrumentation and techniques. More generally this emerging focusing technology may help alleviate the challenges of large-scale synthesis traditionally associated with neutron diffraction. Sample volumes in the sub-100 x 100 x 100 micron range are now becoming feasible for neutron scattering studies. Also, future possibilities of *in situ* characterization during Extreme Environment NanoMaterial Synthesis will be briefly highlighted by showing our recent neutron studies of high pressure magnetic transitions in nanosized particles of hematite (Fe_2O_3).

Structure and Dynamics of Nanostructured Materials

X.-L. Wang, Oak Ridge National Laboratory, and C. T. Liu and T. Egami, Oak Ridge National Laboratory and University of Tennessee

Neutron and synchrotron x-ray are great tools for probing the bulk behavior of a material, and nanostructured materials are no exception. With the advent of powerful sources and the scattering instrumentation, *in situ*, time-resolved experiments are becoming a reality. These experiments will play a crucial role in elucidating the structure and dynamics at nanoscale.

Our research in nano science encompasses three areas: (1) Deformation mechanisms in nanostructured materials, (2) Phase transformation at nanoscale, (3) Structure and thermal stability of self-assembed nanoclusters in metallic matrices. Highlights from recent experiments will be presented.

This research is supported by Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

Applications of Electron Microscopy for Discovery, Understanding and Property Measurements of Oxide Nanostructures

Zhong Lin (ZL) Wang, Georgia Institute of Technology

Nanowire- and nanotube-based materials have been demonstrated as building blocks for nanocircuits, nanosystems, and nanooptoelectronics. Quasi-one-dimensional nanostructures (so called nanobelts or nanoribbons) have been successfully synthesized for semiconducting oxides of zinc, tin, indium, cadmium and gallium, by simply evaporating the desired commercial metal oxide powders at high temperatures [1]. The belt-like morphology appears to be a unique and common structural characteristic for the family of semiconducting oxides with cations of different valence states and materials of distinct crystallographic structures. Using the technique demonstrated for measuring the mechanical properties of carbon nanotubes based on *in situ* transmission electron microscopy [2,3,4], the bending modulus of the oxide nanobelts, the workfunction at the tip have been measured. Field effect transistors [6] and ultra-sensitive nanosize gas sensors [7], nanoresonators and nanocantilevers [8] have also been fabricated based on individual nanobelts. Thermal conductivity of a nanobelt has also been measured. Very recently, nanobelts, nanorings, and nanosprings that exhibit piezoelectric properties have been synthesized, which are potential candidates for nanoscale traducers, actuators, and sensors [9,10,11,12]. This presentation will focus on our recent progress in the controlled growth, nanoscale property measurements, and nanosize device fabrication using oxide nanostructures that are semiconducting and piezoelectric. Research sponsored by NSF, NASA, and DARPA. For further details see www.nanoscience.gatech.edu/zlwang.

References

1. Z. W. Pan, Z. R. Dai, Z. L. Wang, Nanobelts of semiconducting oxides, Science **209**, 1947 (2001). doi:10.1126/science.1058120
2. P. Poncharal, Z. L. Wang, D. Ugarte, W. A. de Heer, Electrostatic deflections and electromechanical resonances of carbon nanotubes, Science **283**, 1513 (1999). doi:10.1126/science.283.5407.1513
3. Electron Microscopy of Nanotubes, ed. Z. L. Wang and C. Hui, Kluwer Academic (2003).
4. R. P. Gao, Z. L. Wang, Z. G. Bai, W. de Heer, L. Dai, M. Gao, Nanomechanics of individual carbon nanotubes from pyrolytically grown arrays, Phys. Rev. Lett. **85**, 622 (2000). doi:10.1103/PhysRevLett.85.622
5. Z. L. Wang, P. Poncharal,W. A. De Heer, Nanomeasurements of individual carbon nanotubes by in situ TEM, Pure Appl. Chem. Vol. **72** (2000). doi:10.1351/pac200072010209
6. M. Arnold, P. Avouris, Z. W. Pan, Z. L. Wang, Field-effect transistors based on single semiconducting oxide nanobelts, Phys. Chem. B **107**, 659 (2002). doi:10.1021/jp0271054
7. E. Comini, G. Faglia, G. Sberveglieri, Z. W. Pan, Z. L. Wang, Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts, Appl. Phys. Lett. **81**, 1869 (2002). doi:10.1063/1.1504867
8. W. Hughes, Z. L. Wang, Nanobelts as nanocantilevers, Appl. Phys. Lett. **82**, 2886 (2003). doi:10.1063/1.1570497

9. X. Y. Kong, Z. L. Wang, Spontaneous polarization-induced nanohelixes, nanosprings, and nanorings of piezoelectric nanobelts, Nano Lett. **2**, 1625 (2003). doi:10.1021/nl034463p
10. Z. L. Wang, X. Y. Kong, J. M. Zuo, Induced growth of asymmetric nanocantilever arrays on polar surfaces, Phys. Rev. Lett. **91**, 185502 (2003). doi:10.1103/PhysRevLett.91.185502
11. "Nanowires and Nanobelts – materials, properties and devices; Vol. I: Metal and Semiconductor Nanowires," Vol. II: Nanowires and Nanobelts of Functional Materials," edited by Z. L. Wang, Kluwer Academic (2003).
12. X. Y. Kong, Y. Ding, R. S. Yang, Z. L. Wang, Single-crystal nanorings formed by epitaxial self-coiling of polar nanobelts, Science **303**, 1348 (2004). doi:10.1126/science.1092356

Characterization of the Surfaces of Nanostructures Using Positron Annihilation Induced Auger and Gamma Spectroscopies

Alex Weiss, University of Texas at Arlington

Experiments performed at the University of Texas at Arlington have demonstrated that Positron annihilation induced Auger spectroscopy (PAES) is capable of characterizing the elemental content and structure of the topmost atomic layer with single atomic layer resolution and have shown its ability to eliminate the secondary electron background. [1] Here we present experimental and theoretical results that indicate that positrons will trap with high efficiency in surface states localized on top of surface nanostructures. We propose to exploit this effect by developing and applying new site-specific spectroscopic tools for characterizing the elemental content and electronic structure of surface nanostructures. The elemental content of the top most layer of the nanostructure will be determined from the PAES spectra resulting from the annihilation of a positron in this surface state. In addition, information regarding the electronic structure at the surface of the nanostructure will be obtained from the energy spectra of Doppler-broadened annihilation gamma rays. The localization of positrons on top of the nano structures will allow us to selectively probe the nanostructures without interference from signals from the substrate material.

References

1. D. Mehl, A.R. Köymen, K.O. Jensen, F. Gotwald, and A. Weiss, Sensitivity of positron-annihilation-induced Auger-electron spectroscopy to the top surface layer, *Phys. Rev. B* **41**, 799–802 (1990). doi:10.1103/PhysRevB.41.799

X-ray Imaging at Nanometer Scale: Opportunities and Challenges

W. Yun, Xradia, Inc.

X-ray imaging offers important and desirable visualization and characterization capabilities for nanoscience and nanotechnology. For example, its short wavelength permits nanometer resolution imaging without the limitation of wavelength. Its high penetration power allows nondestructive imaging of internal structures of an object. It has many contrast mechanisms that can be employed beyond simple structural imaging, such as chemical state imaging or elemental specific imaging. To realize the potential of x-ray imaging with nanometer scale resolution, there are significant challenges. In my presentation, I will present a theoretical framework why x-ray imaging with nanometer scale resolution is achievable and discuss the technical challenges that need to be overcome.

Appendix B. Agenda

	Thursday, June 16, 2005	
7:30 am – 8:00 am	Continental Breakfast	Blue Room Prefunction
8:00 am – 8:15 am	**Welcome and Charge** Kristin Bennett, Basic Energy Sciences	Blue Room
8:15 am – 8:45 am	**Nanotechnology – Where We Are Headed….** Jack Marburger, III, Office of Science and Technology Policy	Blue Room
8:45 am – 9:15 am	**Visualizing the Nanoscale: The Role of X-ray and Neutron Scattering** Patricia Dehmer, Basic Energy Sciences	Blue Room
9:15 am – 9:45 am	**X-ray and Neutron Scattering Facilities: A National Policy Perspective** Pat Looney, Office of Science and Technology Policy	Blue Room
9:45 am – 10:15 am	**Scientific and Technology Challenges for the Nanotechnology Community** Clayton Teague, National Nanotechnology Coordination Office **National Nanotechnology Initiative from a Policy Perspective** Celia Merzbacher, Office of Science and Technology Policy	Blue Room
10:15 am – 10:30 am	Break	Blue Room Prefunction
	Nanotechnology –What Are the Challenges for Scattering Research Session Chair: Linda L. Horton, Oak Ridge National Laboratory	Blue Room
10:30 am – 11:00 am	**Biological Applications and Opportunities for Nanoscience** Carolyn Larabell, University of California,San Francisco	Blue Room
11:00 am – 11:30 am	**X-ray Studies of the Nanoworld – Motivation, Concepts and Applications** Jo Stöhr, Stanford Synchrotron Radiation Laboratory	Blue Room
11:30 am – noon	**Patterned Nanoscale Materials** Teri Odom, Northwestern University	Blue Room
noon – 12:30 pm	**Small Is Different: Emergent Behavior in the Nanoscale** Uzi Landman, Georgia Institute of Technology	Blue Room
12:30 pm – 1:30 pm	Lunch	Blue Room Prefunction
1:30 pm – 4:30 pm Blue Room Breakout Session 1A **Synthesis** – co-chairs Phillip Britt, ORNL; and Robert Hull, UVa	1:30 pm – 4:30 pm Congressional A Breakout Session 1B. **Directed and Self Assembly** – co-chairs Eric Kaler, U Delaware; and Youli Li, UCSB	1:30 pm – 4:30 pm Congressional B Breakout Session 1C. **Novel Properties** – co-chairs – D. Wayne Goodman, Texas A&M; and Eric Fullerton, Hitachi Global Storage Technologies
1:30 pm – 2:00 pm 1A **Synthesis and Characterization of Novel Polymer Architectures** – Phillip Britt, ORNL	1:30 pm – 2:00 pm 1B**. X-rays and Neutrons for Directed and Self-Assembly** – Eric Kaler, U Delaware	1:30 pm – 2:00 pm 1C. **Catalysis by Metal Nanoclusters** – Wayne Goodman, Texas A&M
2:00 pm – 2:30 pm 1A. **Advanced Characterization Needs for Epitaxially Grown Nanostructures** – Robert Hull, UVa	2:00 pm – 2:30 pm 1B. **Small Angle X-ray Scattering/ Diffraction of Supramolecular Assemblies** – Youli Li, UCSB	2:00 pm – 2:30 pm 1C. **Nanostructured magnetic materials: novel physics and emerging technologies** – Eric Fullerton, Hitachi Global Storage Technologies
2:45 pm – 3:00 pm	Break	Blue Room Prefunction, Congressional Foyer
2:45 pm – 4:30 pm Blue Room 5 minute presentations from participants in Breakout Session #1A and discussion	2:45 pm – 4:30 pm Congressional A 5 minute presentations from participants in Breakout Session #1B and discussion	2:45 pm – 4:30 pm Congressional B 5 minute presentations from participants in Breakout Session #1C and discussion
5:00 pm – 6:00 pm	Reception (cash bar)	Hampton
6:00 pm – 7:30 pm	Dinner	Hampton
7:30 pm – 9:00 pm	**The Future Is Ours!** Poster presentations by early career scientists Session Chairs: Takeshi Egami, University of Tennessee and Ian S. Anderson, Oak Ridge National Laboratory	Congressional A and B Cash bar (beer and wine)

Friday, June 17, 2005		
7:30 am – 8:00 am	Continental Breakfast	Blue Room Prefunction
8:00 am – 8:05 am	**Welcome and Day 2 Charge** Paul Nealey, University of Wisconsin-Madison	Blue Room
8:05 am – 9:30 am	**What Experiments** Does The **Future of Nanoscience Depend Upon: Summary of The prior Day's Discussions** by Break-out Session Chairs	Blue Room
9:30 am – 9:45 am	Break	Blue Room Prefunction
	Scattering Techniques to Meet the Nanoscale Research Challenges: Extraordinary Tools for Extraordinary Science Session Chair: Mark Ratner, Northwestern University	Blue Room
9:45 am – 10:15 am	**Opportunities for Nanoscience with X-rays** Eric Isaacs, Argonne National Laboratory and University of Chicago	Blue Room
10:15 am – 10:45 am	**Scientific Opportunities with Synchrotron Radiation for Nanoscience,** Zahid Hussain, Lawrence Berkeley National Laboratory	Blue Room
10:45 am – 11:15 am	**Advanced Instrumentation for Neutron Scattering Studies of Nanoscale Materials,** Roger Pynn, Los Alamos National Laboratory	Blue Room
11:15 am – 11:45 am	**Marrying Reaction Chemistry to Surfaces,** Colin Nuckolls, Columbia University	Blue Room
11:45 am – 12:15 pm	**Relevance of Strong Electronic Correlations in Bulk and Nano Systems,** Elbio Dagotto, University of Tennessee	Blue Room
12:15 pm – 1:15 pm	Lunch	Blue Room Prefunction
1:45 pm- 4:30 pm Blue Room Breakout Session #2A. **Advanced Technique Development** – co-chairs: Roland Gähler, ILL; and Wenbing Yun, Xradia, Inc.	1:45 pm- 4:30 pm Blue Room Prefunction Breakout Session #2B. **Advanced Characterization for Nanomaterials** – co-chairs: Gabrielle Long, ANL; and Dan Neumann, NIST	1:45 pm- 4:30 pm Capitol Breakout Session #2C. **Theory and Modeling** – co-chairs: Grant Smith, U Utah; and Philip Pincus, UCSB
1:45 pm – 2:15 pm **2A. Neutrons and Nanoscience – Some Scientific and Instrumental Perspectives** – Roland Gähler, ILL	1:45 pm – 2:15 pm 2B. **Nanomaterials Science at the APS** – Gabrielle Long, ANL	1:45 pm – 2:15 pm 2C. **Synergism of Neutron Scattering and Molecular Simulations in Understanding Dynamics and Structure of Polymer-Based Nanomaterials** – Grant Smith, U Utah
2:15 pm – 2:45 pm **2A. X-ray Imaging at Nanometer Scale: Opportunities and Challenges –** Wenbing Yun, Xradia, Inc.	2:15 pm – 2:45 pm 2B. **Neutron Methods for Nanotechnology** – Dan Neumann, NIST	2:15 pm – 2:45 pm 2C. **Functional Bio-nano Molecular Materials: Is there Something to Learn from Mother Nature?** – Philip Pincus, UCSB
2:45 pm – 3:00 pm	Break	Blue Room Prefunction
3:00 pm – 4:30 pm Blue Room 5 minute presentations from participants in Breakout Session #2A and discussion	3:00 pm – 4:30 pm Blue Room Prefunction 5 minute presentations from participants in Breakout Session #2B and discussion	3:00 pm – 4:30 pm Capitol 5 minute presentations from participants in Breakout Session #2C and discussion
4:30 pm – 7:00 pm	Dinner (on own)	
7:00 pm – 8:30 pm	**What New Capabilities will Developments in Scattering Techniques Bring to Nanoscience?: Summary of the afternoon discussions** by Breakout Session Chairs Session Chair: Eric Isaacs, Argonne National Laboratory and University of Chicago	Blue Room Prefunction Cash bar
	Saturday, June 18, 2005 – By Invitation only Organizers, Discussion Leaders, and Scribes only-Report Writing 8:30 am– 3:00 pm	8:00 am – 8:30 am Breakfast…..Capitol

Appendix C. Participants

Thomas G. Aigner
National Institutes of Health, National Institute on Drug Abuse

Yvonne Akpalu
Rensselaer Polytechnic Institute

Dirar Al Homouz
University of Houston

Cate Alexander
National Nanotechnology Coordination Office

Paul Alivisatos
University of California, Berkeley

Ian M. Anderson
Oak Ridge National Laboratory

Ian S. Anderson
Oak Ridge National Laboratory

Meigan Aronson
Michigan State University

Robert Astheimer
U.S. Department of Energy

Sam Bader
Argonne National Laboratory

Barbara A. Baird
Cornell University

James R. Baker, Jr.
The University of Michigan

Robert S. Balaban
National Institutes of Health, National Heart, Lung, and Blood Institute

Tim Baldwin
National Institutes of Health, National Institute of Biomedical Imaging and Bioengineering

Kristian Baumann
Institut Laue-Langevin

Mike Bedzyk
Northwestern University

M. Kathleen Behrens
RS Investments (representing the President's Council of Advisors on Science and Technology)

Angela M. Belcher
Massachusetts Institute of Technology

Kristin A. Bennett
U.S. Department of Energy

Sangeeta N. Bhatia
University of California, San Diego

Simon Billinge
Michigan State University

Kwabena A. Boahen
University of Pennsylvania

Kristina Boehlke
German Ministry of Education and Research

Katherine Borden
Mount Sinai School of Medicine

Daniel Branton
Harvard University

Harold Bright
Office of Naval Research

John Brighton
National Science Foundation

Phil Britt
Oak Ridge National Laboratory

Joel Brock
Cornell University

Thomas F. Budinger
Lawrence Berkeley National Laboratory

Denis Buxton
National Institutes of Health, National Heart, Lung, and Blood Institute

Marie-France Carlier
CNRS, France

Linda Cerrone
U.S. Department of Energy

Christopher S. Chen
Johns Hopkins University

Hongda Chen
U.S. Department of Agriculture

Yong Chen
Princeton University/ NHMFL

Yuan Chen
Yale University

Chil-Hung Cheng
Texas A&M University

Linda Chrisey
Office of Naval Research

Dean A. Cole
U.S. Department of Energy

Vicki Colvin
Rice University

Edward C. Cox
Princeton University

Elbio Dagotto
University of Tennessee

Pat Dehmer
U.S. Department of Energy

Mrinal K. Dewanjee
National Institute of Standards and Technology

Robert Dimeo
National Institute of Standards & Technology

Norm J. Dovichi
University of Washington

Michael L. Dustin
New York University School of Medicine

Takeshi Egami
University of Tennessee

Al Ekkebus
Oak Ridge National Laboratory

Angela Ervin
Office of Naval Research

Paul Evans
University of Wisconsin-Madison

Kenneth Evans-Lutterodt
Brookhaven National Laboratory

Lixin Fan
Argonne National Laboratory

Brad Fenwick
U.S. Department of Agriculture

Millie Firestone
Argonne National Laboratory

Zach Fisk
University of California Davis

Timothy Fitzsimmons
U.S. Department of Energy

Dillon Fong
Argonne National Laboratory

Joanna Fowler
Brookhaven National Laboratory

Eric Fullerton
Hitachi Global Storage Technologies

Roland Gähler
Institut Laue-Langevin

Pat Gallagher
National Institute of Standards & Technology

Oleg Gang
Brookhaven National Laboratory

Gradimir Georgevich
National Institute of Standards and Technology

Henry Glyde
University of Delaware

Wayne Goodman
Texas A&M University

Stephen B. Gould
National Nanotechnology Coordination Office

Alexei Grigoriev
University of Wisconsin-Madison

Jay T. Groves
University of California, Berkeley

Rolf Gruetter
University of Minnesota

Peixuan Guo
Purdue University

Bruce Hamilton
National Science Foundation

Todd Harding
Office of the Director

Joan Harmon
National Institutes of Health, National Institute of
Biomedical Imaging and Bioengineering

Frederick Heineken
National Science Foundation

Michael Heller
University of California, San Diego

Russell J. Hemley
Carnegie Institution

Maryanna P. Henkart
National Science Foundation

Geoffrey M. Holdridge
National Nanotechnology Coordination Office

Linda Horton
Oak Ridge National Laboratory

James Horwitz
U.S. Department of Energy

Matthew A. Howard
University of Iowa

Jan Hrbek
Brookhaven National Laboratory

Tobias Huerlimann
Institut Laue-Langevin

Robert Hull
University of Virginia

Zahid Hussain
Lawrence Berkeley National Laboratory

Robert Hwang
Brookhaven National Laboratory

Gene Ice
Oak Ridge National Laboratory

Yves Idzerda
Montana State University

Donald E. Ingber
Harvard Medical School

Steven Irizarry
Office of Senator Judd Gregg

Eric Isaacs
Argonne National Laboratory

Althea Jones
National Science Foundation

Eric Kaler
University of Delaware

Sudesh Kamath
University of Tennessee

Barbara P. Karn
Environmental Protection Agency

Christine Kelley
National Institutes of Health, National Institute of Biomedical Imaging and Bioengineering

Richard D. Kelley
U.S. Department of Energy

Helen Kerch
U.S. Department of Energy

Rajinder Khosla
National Science Foundation

Ginam Kim
Dow Corning

Aravinda M. Kini
U.S. Department of Energy

Roger Klaffky
U.S. Department of Energy

Dale Koelling
U.S. Department of Energy

Brenda Korte
National Institutes of Health, National Institute of Biomedical Imaging and Bioengineering

Eleni Kousvelari
National Institutes of Health, National Institute of Dental and Craniofacial Research

Kathryn Krycka
State University of New York at Stony Brook

Harriet Kung
U.S. Department of Energy

Alex Lacerda
Los Alamos National Laboratory

Uzi Landman
Georgia Institute of Technology

Carolyn Larabell
University of California, San Francisco

John Larese
University of Tennessee

Charlie Laub
University of California, Los Angeles

Chris Leighton
University of Minnesota

Paul C. Letourneau
University of Minnesota

Catherine Lewis
National Institutes of Health, National Institute of General Medical Sciences

Laura H. Lewis
Brookhaven National Laboratory

Youli Li
University of California, Santa Barbara

Frances Ligler
Naval Research Laboratory

Soo-Siang Lim
National Science Foundation

Philip Lippel
National Nanotechnology Coordination Office

Jennifer Lippincott-Schwartz
National Institutes of Health, National Institute of Child Health and Human Development

Rodolfo Llinas
New York University

Gabrielle Long
Argonne National Laboratory

Pat Looney
Office of Science & Technology Policy

Mathias Lősche
Johns Hopkins University

Doug Lowndes
Oak Ridge National Laboratory

Carol Lucas
National Science Foundation

Martha Lundberg
National Institutes of Health,
National Heart, Lung, and Blood Institute

Peter Lyster
National Institutes of Health, National Institute of Biomedical Imaging and Bioengineering

Lee Magid
National Science Foundation

Derrick C. Mancini
Argonne National Laboratory

Jack Marburger
Office of Science & Technology Policy

Marie Markarian
Florida State University

Donald E. Marlowe
U.S. Food and Drug Administration

Michael Marron
National Institutes of Health,
National Center for Research Resources

Paul Maupin
U.S.Department of Energy

Larry V. McIntire
Georgia Institute of Technology

Thomas J. Meade
Northwestern University

Ammanuel Mehreteab
Colgate-Palmolive

Todd Merchak
National Institutes of Health, National Institute of
Biomedical Imaging and Bioengineering

Celia Merzbacher
Office of Science & Technology Policy
National Science and Technology Council

John Miao
University of California, Davis

Terry A. Michalske
Sandia National Laboratories

Paul Miceli
University of Missouri-Columbia

Raul Miranda
U.S. Department of Energy

Edward Monachino
National Institutes of Health, National Cancer Institute

Pedro Montano
U.S. Department of Energy

Carlo D. Montemagno
University of California, Los Angeles

James S. Murday
Naval Research Laboratory

Steven Nagler
Oak Ridge National Laboratory

Heinrich Nakotte
New Mexico State University

Paul Nealey
University of Wisconsin

Daniel Neumann
National Institute of Standards & Technology

Colin Nuckolls
Columbia University

James Oberhauser
University of Virginia

Teri Odom
Northwestern University

Bill Oosterhuis
U.S. Department of Energy

John A. Parrish
Harvard University

Nicholas A. Peppas
University of Texas at Austin

Dmitri Petrovykh
Naval Research Laboratory

Roderic I. Pettigrew
National Institutes of Health, National Institute of
Biomedical Imaging and Bioengineering

Chinh H. Pham
Greenberg Traurig, LLP

Michael E. Phelps
University of California, Los Angeles

Phil Pincus
University of California, Santa Barbara

Ron Pindak
Brookhaven National Laboratory

Michael T. Postek
National Institute of Standards and Technology

Danilo Pozzo
Carnegie Mellon University

Yevgeniy Puzyrev
Florida Atlantic University

Roger Pynn
Los Alamos National Laboratory/ Indiana University

Mark Ratner
Northwestern University

Anna Retzke
National Institutes of Health, National Institute of
Biomedical Imaging and Bioengineering

Jim Rhyne
Los Alamos National Laboratory

Rebecca Richards-Kortum
University of Texas at Austin

Mihail C. Roco
National Science Foundation and
National Science and Technology Council

Mike Roco
National Science Foundation

Merlyn Rodrigues
National Institutes of Health, National Library of Medicine

Marie-Louise Saboungi
Université d'Orléans

Marc Salit
National Institute of Standards and Technology

Jeffery A. Schloss
National Institutes of Health, National Human Genome Research Institute

Ivan Schuller
University of California, San Diego

Klaus Schulten
University of Illinois

Thomas Schulthess
Oak Ridge National Laboratory

Norm R. Scott
Cornell University

Gerald Selzer
National Science Foundation

Robert Shannon
House Ear Institute

Michael P. Sheetz
Columbia University

Hirohiko Shimizu
RIKEN

Nancy L. Shinowara
National Institutes of Health, National Institute of Child Health and Development

Eric Shirley
National Institute of Standards & Technology

Michael L. Shuler
Cornell University

Robert Shull
National Institute of Standards & Technology

Paul A. Sieving
National Institutes of Health, National Eye Institute

Mike Simonson
Oak Ridge National Laboratory

Michael L. Simpson
Oak Ridge National Laboratory

Subodh Singh
Sinte Gleska University

Grant Smith
University of Utah

Greg Smith
Oak Ridge National Laboratory

Malcolm L. Snead
University of Southern California

Yeong-ah Soh
Dartmouth University

Patricia M. Sokolove
National Institutes of Health, National Institute of Biomedical Imaging and Bioengineering

Peter Stair
Northwestern University

Patrick S. Stayton
University of Washington

G. Brian Stephenson
Argonne National Laboratory

Walter Stevens
U.S. Department of Energy

Jo Stohr
Stanford Synchrotron Radiation Laboratory

Matthew Stone
Oak Ridge National Laboratory

Joe Strzalka
University of Pennsylvania

Samuel I. Stupp
Northwestern University

Richard Swaja
National Institutes of Health, National Institute of Biomedical Imaging and Bioengineering

Jonathan V. Sweedler
University of Illinois

Karen Talamini
U.S. Department of Energy

E. Clayton Teague
National Nanotechnology Coordination Office

Suzanne TeVelthius
Argonne National Laboratory

Guebre X. Tessema
National Science Foundation

K. Thirumalai
Department of Transportation

Matthew Tirrell
University of California, Santa Barbara

Roger Y. Tsien
University of California, San Diego

Chris Tulk
Oak Ridge National Laboratory

Linda Turner
Harvard University

Victor Turner
National Nanotechnology Coordination Office

Judith Vaitukaitis
National Institutes of Health,
National Center for Research Resources

Anil Verma
American Board of Internal Medicine

Viola Vogel
University of Washington

Thomas Vogt
Brookhaven National Laboratory

Larry Walker
Cornell University

David R. Walt
Tufts University

Kuan Wang
National Institutes of Health, National Institute of Arthritis and Musculoskeletal and Skin Diseases

Xun-li Wang
Oak Ridge National Laboratory

Chiming Wei
Johns Hopkins University School of Medicine

Alex Weiss
University of Texas-Arlington

Harry WestfahlJr
Brazilian Synchrotron Light Source

Catherine Woytowicz
U.S. Department of State

Ting Xu
University of Pennsylvania

Kenneth M. Yamada
National Institutes of Health, National Institute of Dental and Craniofacial Research

Wenbing Yun
Xradia, Inc.

APPENDIX D. EARLY CAREER SCHOLARS

The participants selected for the early career poster session are listed subsequently with their affiliations and the title (in bold type) of the poster that was shown during the workshop. The participants in this session represented a mix of undergraduate and graduate students, postdoctoral fellows, and young faculty.

Figure D.1. Early Career Poster Session winners: 17 early career scientists- graduate students, postdocs, and recently appointed faculty members- pose during the scholarship award ceremony with Agency and Institute representatives T. Egami (JINS) and G. Tessema (NSF) during the presentation ceremony prior to the evening poster session. (Courtesy Kristin Bennett, EPSCoR, Office of Science, U.S. Department of Energy).

Yvonne Akpalu, Rensselaer Polytechnic Institute, *Integrated Light, X-ray and Neutron Scattering: An Approach Towards Advancing Renewable Materials*

Yong Chen, Princeton University/NHMFL, *Nano Meets Macro: Correlated Phases and Collective Dynamics—Out-of-box "Scattering" Opportunities*

Yuan Chen, Yale University, *In Situ Absorption Characterization of Nano Metallic Clusters During Single Wall Carbon Nanotube Synthesis*

Chil-Hung Cheng, Texas A&M University, *Investigation of High-Silica Zeolite Nucleation with High Flux X- ray/ Neutron Small Angle Scattering*

Paul Evans, University of Wisconsin-Madison, *Structural and Magnetic X-ray Microscopy for Nanoscience*

Lixin Fan, Argonne National Laboratory, *Characterization of Medium-Range Order in Nanocrystalline Systems by Fluctuation X-ray Microscopy*

Dillon Fong, Argonne National Laboratory, *In Situ X-ray Phase Transition Studies of Phase Transitions*

Alexei Grigoriev, University of Wisconsin-Madison, *Time Resolved X-ray Microdiffraction: Probing Dynamics on Nanoscale*

Sudesh Kamath, University of Tennessee, *Dynamics in Multicomponent Polymer Systems*

Kathryn Krycka, State University of New York at Stony Brook, *Anomalous Small Angle Scattering Study of Nanomagnetic Materials*

Marie Markarian, Florida State University, *Stimulus-Induced Disordering in Soft Layered Nanocomposites*

James Oberhauser, University of Virginia, *Flow-Induced Crystallization of Isotactic Polypropylene: The Role of Long Chains and Molecular Architecture*

Danilo Pozzo, Carnegie Mellon University, *Block-Copolymer Templated Nanocomposites: Structure Manipulation of Nanoparticles and Proteins*

Yevgeniy Puzyrev, Florida Atlantic University, *Local Atomic Displacements in Cu85.2Al14.8 Alloy*

Matthew Stone, Oak Ridge National Laboratory, *Magnetic Neutron Scattering: An Essential Probe of NanoMagnetism*

Joe Strzalka, University of Pennsylvania, *Enhancing the Sensitivity of X-ray and Neutron Reflectivity to Sub-Molecular Features within the Profile Structure of Synthetic Protein Monolayers at the Air/Water Interface*

Ting Xu, University of Pennsylvania and NIST, *Design, Synthesis and Characterization of Artificial Proteins for Biomolecular Material*

APPENDIX E. GLOSSARY

1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional
ab initio	from first principles
AFM	atomic force microscopy
ALS	Advanced Light Source, Lawrence Berkeley National Laboratory
AND/R	Advanced Neutron Reflectometer and Diffractometer
APS	Advanced Photon Source, Argonne National Laboratory
BEC	Bose-Einstein condensation
CAMD	Center for Advanced Microstructures & Devices, Louisiana State University
CAT	computed axial tomography
CHESS	Cornell High Energy Synchrotron Source, Cornell University
CMR	colossal magnetoresistance
CNBT	Cold Neutrons in Biology and Technology (symposium)
CNM	Center for Nanoscale Materials, Argonne National Laboratory
CRL	compound refractive lens
DOE	Department of Energy
DINS	Deep Inelastic Neutron Scattering
DMTA	dynamic mechanical thermal analysis
EPR	electron paramagnetic resonance
ERL	energy recovery linac
EUV	extreme ultraviolet
EXAFS	extended x-ray absorption fine structure
FEL	free electron laser
GaN	gallium nitride
GISAXS	grazing incidence small-angle scattering
GMR	giant magnetoresistance
HFIR	High Flux Isotope Reactor Center for Neutron Scattering, Oak Ridge National Laboratory
IPNS	Intense Pulsed Neutron Source, Argonne National Laboratory
IR	infrared
JAERI	Japan Atomic Energy Research Institute
KB	Kirkpatrick-Baez
LANSCE	Los Alamos Neutron Science Center, Los Alamos National Laboratory
LCLS	Linac Coherent Light Source
LEEM	low-energy electron microscopy
MBE	molecular beam epitaxy
MCD	magnetic circular dichroism

MD	molecular dynamics
MLD	magnetic linear dichroism
MWCNT	multiwall carbon nanotubes
MOCVD	metal organic chemical vapor deposition
NCNR	NIST Center for Neutron Research, National Institute of Standards and Technology
NIH	National Institutes of Health
NIST	National Insitute of Standards and Technology
NMR	nuclear magnetic resonance
NNCO	National Nanotechnology Coordination Office
NNI	National Nanotechnology Initiative
NR	neutron radiography
NSET	Nanoscale Science, Engineering, and Technology (Subcommittee of the NSTC Committee on Technology)
NSF	National Science Foundation
NSLS	National Synchrotron Light Source, Brookhaven National Laboratory
NSTC	Natioanl Science and Technology Council
NT	neutron tomography
PAES	positron-annihilation-induced Auger electron spectroscopy
PDF	pair distribution function
PEEM	photoemission electron microscopy
PLD	pulsed laser deposition
PNR	polarized neutron reflectometry
QDs	quantum dots
RF	radio frequency
SANS	small-angle neutron scattering
SAS	small-angle scattering
SAXS	small-angle x-ray scattering
SAXD	small-angle x-ray diffraction
SEXAFS	surface extended x-ray absorption fine structure
SCE	strongly correlated electrons
SEM	scanning electron microscopy
SNS	Spallation Neutron Source, Oak Ridge National Laboratory
SRC	Synchrotron Radiaion Center, University of Wisconsin-Madison
STM	scanning tunneling microscopy
TEM	transmission electron microscopy
TR-XRD	time-resolved x-ray diffraction
USAXS	ultra-small-angle x-ray scattering
UV	ultraviolet
VUV	vacuum ultraviolet

XAFS	x-ray absorption fine structure
XANES	x-ray absorption near-edge spectroscopy
XAS	x-ray absorption spectroscopy
XEOL	x-ray-excited optical luminescence
XPEEM	x-ray photoemission electron microscopy
XPS	x-ray photoelectron spectroscopy
XRIM	x-ray reflection interfacial microscopy
XRF	x-ray fluorescence
XRR	x-ray reflectivity
XSW	x-ray standing wave

National Science and Technology Council
Committee on Technology

Subcommittee on Nanoscale Science, Engineering, and Technology

National Nanotechnology Coordination Office
4201 Wilson Blvd.
Stafford II, Rm. 405
Arlington, VA 22230

703-292-8626 phone
703-292-9312 fax

www.nano.gov

X-RAYS AND NEUTRONS: ESSENTIAL TOOLS FOR NANOSCIENCE RESEARCH

NNI WORKSHOP