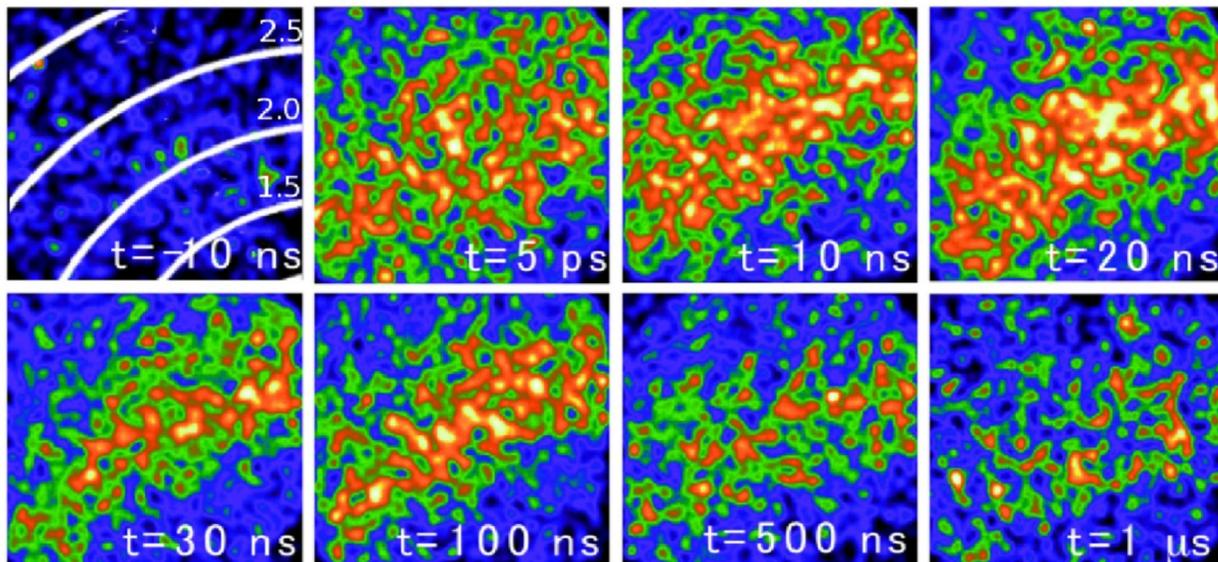# Evolution and Control of Complexity: Key Experiments Using Sources of Hard X-rays

*A Report of a Workshop held October 11-13, 2010*

## Advanced Photon Source

**Cover**

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Resolution, A.M. Lindenberg, et.al., Physical Review Letters 100, 135502 (2008)

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# Evolution and Control of Complexity:
# Key Experiments Using Sources of Hard X-rays

*A Report of a Workshop held October 11-13, 2010*

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# *Executive Summary*

Nature in its every manifestation exhibits far-away-from-equilibrium processes, leading to complexity of orders. The majority of processes in nature demonstrate nonlinear behavior that obeys non-equilibrium thermodynamics from the flow of energy. This is also true of most of the processes involved in modern-day technologies, from information storage to energy conversion, and from catalysis to medical devices to materials synthesis. Hence, there is a universal interest in understanding the non-equilibrium processes resulting from optimized energy flows. How does the local order of higher complexity develop over time starting from an initial state of complete chaos formed from a sudden influx of energy? Is there a unifying theme that governs the processes behind the evolution of order from sub-Ångstrom to mesoscopic scales? How can these processes be optimally controlled?

This is the first workshop to collectively address the above questions in the context of new developments in hard x-ray sources. The *core questions* centered around two topics:

(a) Control of the flow of energy to the system achieved by selecting an energy pump with suitable characteristics (pH, T-pulse, wavelength, polarization, coherence, pulse width, intensity, etc.), and

(b) interrogation of the space-time evolution of the system from sub-Ångstrom to mesoscopic details using an appropriate hard x-ray spatiotemporal tool with suitable space and time resolution.

Against this background, a workshop to explore "Evolution and Control of Complexity: Key Experiments Using Sources of Hard X-rays" was convened at Argonne National Laboratory in October 2010. This workshop was attended by approximately 150 international science and engineering leaders in condensed matter physics, chemical science, biological science, soft matter, computational science, engineering, and the technologies related to these fields along with developers of x-ray and laser sources and instrumentation. While a number of recent workshops have recognized the challenge of time-domain applications using hard x-rays, none have focused on the two topics mentioned above, which are at the core of non-equilibrium science.

In the last decade, much progress has been made in the development of hard x-ray sources and tools. This workshop addressed the current state of development of compact sources (CS), storage-ring (SR) sources, energy-recovery linac (ERL) sources, and x-ray free-electron-laser (XFEL) sources. Their characteristics are well suited to *measure the spatiotemporal evolution* of dissipative structures in complex systems with the highest precision (with a temporal resolution of femtosecond to s and spatial resolution from sub-Ångstrom to mesoscopic scales), when integrated with suitable energy excitation capabilities (pumps), x-ray optics, and detectors.

This report provides adequate background to the area of non-equilibrium science, probes unexplored opportunities in this emerging field, and establishes the suitability of new capabilities of hard x-ray sources to probe complex systems. The report includes discussions from focus panels that addressed the core questions on the temporal evolution and control of electronic and chemical

structures in molecular systems, nanostructures, engineering devices, catalysts, biological systems, fluids, and in quantum optics. The topics of focus panels were:

1. *Control of Complex Processes in Condensed Systems*
2. *Controlling the Dynamics of Materials Processing*
3. *Non-equilibrium Chemical Reactions*
4. *Controlling Biological Functions*
5. *Dynamics in Soft Matter and Fluidics*
6. *Nonlinear X-ray Science, X-ray Quantum Optics, and Extreme Metrology*

The real upshot of the anticipated research discoveries in the workshop subject is to develop devices and processes that can significantly improve the quality of life by providing a secure and clean energy future. Furthermore, the applicability of the science of evolution of complex organization can lead our understanding of the mesoscopic frontier.

In the end, the workshop attendees enthusiastically concluded that the goal of learning how to use the non-equilibrium phenomena as skillfully and efficiently as nature does, requires (i) an understanding of the evolution of complex order, (ii) the development of new synthetic systems that mimic nature, (iii) newer energy sources (pumps) and a plethora of optical, infrared, ultraviolet (UV), and hard x-ray sources, and (iv) intensive use of theoretical and computational tools. Discussions on continuing an international effort on the subject area of the workshop, and meeting regularly to discuss progress and future directions was enthusiastically received.

The organizers of the workshop want to thank all the participants, session chairs, focus panel chairs and co-chairs for their hard work in contributing to this report. Special thanks to Helmut Dosch (DESY), Eric Isaacs (ANL), and Jochin Stöhr (SLAC) for their advice and support.

# 1 Background to the Workshop: Understanding the Evolution of Complexity

From the beginning of time to the present, and from the Big Bang to the coming of humankind, nature in its every manifestation has exhibited increasingly complex structural order of varied kinds. Examples of complexity include the self-organization of matter in galaxies, hurricanes, stars, planets, and in prebiotic and cyclical reactions; in living heart, proteins and large molecules, and in glasses; in soft-matter and nanofluidic jets, complex oxides, welds, and in electronic circuits.

How does the organization of higher complexity develop over time starting from a state of complete chaos or non-equilibrium? This question continues to intrigue scientists from a variety of disciplines, from cosmology to biology, because of the underlying common theme of non-equilibrium science and the desire to look for a unifying idea that governs the processes behind the universal order. The evolution of complexity involves spontaneous emergence of spatial, temporal, or spatiotemporal structural organizations of matter over nanoscopic- to mesoscopic- to geological-scales. The new organizations have unique emergent behaviors. To give an extreme example, life itself is an emergent property, which manifests itself when physicochemical systems achieve a specific organization.

The emergent properties of the new matter are beyond the common reductionist description that applied the laws of equilibrium thermodynamics or linear response theory or the Born-Oppenheimer approximation to understand various types of orders in systems. The majority of processes in nature involve nonlinear behavior that obeys non-equilibrium thermodynamics from the flow of energy leading to complexity of order. To develop a precise understanding of the processes involved in the temporal evolution of complexities one has to consider collective dynamical interactions between large numbers of basic units over the mesoscale. A coherent description of the complex order of matter will connect macroscopic behavior to the underlying microscopic interactions utilizing non-equilibrium statistical mechanics.

The complexity has been described in terms of an energy landscape that develops as the non-equilibrium system progresses in time. The energy landscape can have different terrains (flat to rugged) that are typically associated with structurally distinct orders that are separated on the mesoscale [1,2]. The terrain might include separated regions — valleys and sub-valleys of different height — with barriers between them, corresponding to the hills and ridges (**See Box 1**). The individual valleys and sub-valleys in the hierarchical energy landscape are dependent upon a complex set of local parameters, and the interactions between them can only be described based on their statistical topography.

Complexity occurs when the energy minima in the valleys and sub-valleys of the energy landscape are hierarchically spaced. The populated valley or sub-valley in the energy landscape determines the emergent properties of the complex system that are often distinct from the properties of individual valley or sub-valley. The lowest populated minima can be easily changed to a new state through a dynamic or systematic flow of energy to control the landscape and hence the emergent property of the

system with new complexity. All these processes are hence *irreversible*. One may identify two kinds of complex systems:

i) Those systems with energy valleys and sub-valleys that are closely spaced in their *native* environment and these energy states or the landscape can be easily altered by the flow of a *small* amount of energy. For example, several transition metal oxides demonstrate strong electronic correlations resulting from several competing physical interactions— spin, charge, lattice, and/or orbital—that are simultaneously active [3]. This phenomenon causes interesting effects, such as colossal magnetoresistance (CMR), high-temperature superconductivity, nanoscale phase separation, phase transitions, etc. The spontaneous emergence of these properties is associated with the nonlinear interactions between many competing energy states (valleys and sub-valleys). Introduction of lattice inhomogeneities (or composition) and resulting strain fields or an application of external electric or magnetic field or a change in its ambient temperature can easily provide the modest energy flow (10~300 K) required to alter the landscape.

ii) The energy expended in forming the states described by energy valleys and sub-valleys in biological and soft matter is also generally small. For example, in micelle mesophases, the energy landscape depends on various physicochemical parameters, such as pH, ionic strength, and temperature, which change the energy landscape and resulting micelle structure. In fact, a vast majority of soft-matter and biological systems including living systems perform their functions (or processes) when they are driven to conditions that are far away from equilibrium and from a flow of energy [4-6].

iii) The above class of examples represents the systems with which we deal every day; but there are equally interesting systems that have evolved over the $10^{10}$ years since the Big Bang, with the largest energy flow ($10^5$ ~ $10^{12}$ K) and with increasing complexity. Examples include the formation of galaxies, stars, planets, plants, etc. There are also opportunities to create *extreme environments* in which non-equilibrium phases of materials are realized with energy flow of $10^3$ ~ $10^5$ K in a few femtoseconds to microseconds, or with ultrahigh-dynamic pressures. The formation of warm-dense matter, plasma, or processes involved in manufacturing, such as the casting alloys for jet engines, explosion bonding, fabricating nano-features of computer chips, compression of jet sprays, and fabricating high-strength polymers, etc., fall in this class and shows the importance of creating complex matter with emergent properties suitable for industrial applications. This may entail, for example, the use of laser energy pumps, shock waves, ultrahigh electric or magnetic fields from a THz pulse, or GeV-level electron beams.

During the past decade, many of these complex systems have become major areas of research. However, attention has often focused only on deciphering the nature of the complex order after the processes have been completed, thus leaving unfulfilled our understanding of the evolution of the far-away-from-equilibrium processes themselves and the progression of transient stages or the pathways of spatiotemporal order [5].

In spite of the predilection of non-equilibrium behavior in nature and, particularly, in every aspect of our daily activities, fundamental research is lacking on *understanding the processes that predict and control complex order* with precision. After a non-equilibrium-process is set in motion from a flow of energy, the

complex system advances in time by forming a variety of energy valleys and sub-valleys (dissipative structures) that order spontaneously in to self-organized units with increased complexity by exchanging energy with their external environments (**Box 2**). The characteristic length and time scales that describe the evolution of ordered dissipative structures range from sub-Ångstrom sizes to macroscopic and geological measures, an d characteristic formation times from the femtosecond range up to geological periods. **Box 3** explains the progression of self-organization from the evolution of complexity.

The field of complex systems cuts across all traditional disciplines of science as well as engineering. In the context of this workshop, the focus areas of discussion were *processes in condensed systems and materials, reactions in chemical and biological systems, dynamic of fluid flow, non-linear x-ray science; and quantum optics.*

The progress made in the development of hard x-ray sources and tools during the past decade allows us to address key questions on the spatiotemporal evolution of the electronic and structural order in various complex systems in the above focus areas. The spectroscopic, imaging, and structural hard x-ray tools will deliver the required highest precision, either in their *native* environment or when controlled by the *external* flow of energy. This is true whether one is measuring a molecular system, a nanostructure, a chemical reaction, a fabrication process, or a protein unfolding process.

In order to advance our fundamental understanding of non-equilibrium science that will allow us to *predict and control* the evolution of complexity in the above focus areas, we control of the flow of energy to the system and real-time interrogation of the system. These are achieved by selecting an energy pump with suitable characteristics (wavelength, polarization, coherence, pulse width, intensity, field strength, redox, etc.) and utilizing the appropriate *hard x-ray spatiotemporal* tool with suitable space and time resolution. The workshop focus panels inquired as to:

1. The nature of the interactions that lead to complex order or pattern formation from x-ray measurements before and after the evolution of complexity (from a flow of energy),
2. The relationship between the measured emergent properties or behavior and the types of complex order, and
3. Ways to advance the spatiotemporal hard x-ray measurements of the temporal evolution of complex order, from chaos through self-organization or pattern formation, with a controlled flow of energy.

## Box 1: Evolution of Complex Systems: Energy Landscape Far-From-Equilibrium

David Sherrington, "Physics and complexity," Phil. Trans. Roy. Soc. 368, 1175 (2010). In this paper, the evolution of complexity is compared to changes in rugged landscape from an external influence (flow of energy). We quote from this paper:

*" ……. The descriptor 'complex' is used to describe collective behavior that cannot be anticipated simply from the properties of isolated individual units or from interactions among only a few of them, but arises from conflicts when large numbers of individuals have mutually incompletely satisfiable few-body rules, a feature known as 'frustration'; indeed, complex cooperative behavior can arise with even very simple individual units and very simple interactions……."*



*"A 'cartoon' to illustrate the character of a complex system is of a rugged landscape with many hills and valleys and the system's dynamics imagined as movement on the landscape with only local vision, simple moves being downward, becoming stuck in intermediate valleys and unable to surmount ridges, needing a change of rule to overcome them (for example, also allowing uphill moves), only to be faced by further barriers. In fact, the space of the landscape is very high-dimensional and the difficulty extremely much greater than for a mountain range on our three-dimensional Earth. Changing an external influence parameter, such as temperature, magnetic field or other 'pressure', can lead to 'chaotic' transformation of the whole landscape, removing the option of straightforward iteration to a solution."*

## Box 2: Complexity and Energy Rate Density

Eric Chaisson, "Energy Rate Density as a Complexity Metric and Evolutionary Driver," Complexity 16, 27-40 (2011). This paper describes how energy rate density is a single, measurable, and unambiguous quantity that uniformly characterizes varied complex systems, potentially dictating their natural selection on vast spatial and temporal scales. We quote from this paper:

*" ……. Natural selection diagrams schematically illustrate how, at certain critical energies, labeled here variously $E_C$ , systems can spontaneously change, or bifurcate (vertical arrows), into new, non-equilibrium, dynamic steady states. Chance affects the opportunities that arise, but necessity determines which fork systems select, namely which structures and functions are acquired (solid, rising curve) and which become extinct (dashed curves), thus the result is inherently unpredictable as with all of evolution. Such energy-selection diagrams can be drawn for any physical, biological, or cultural system successfully able to adapt and take advantage of increased energy while further complexifying. ….."*
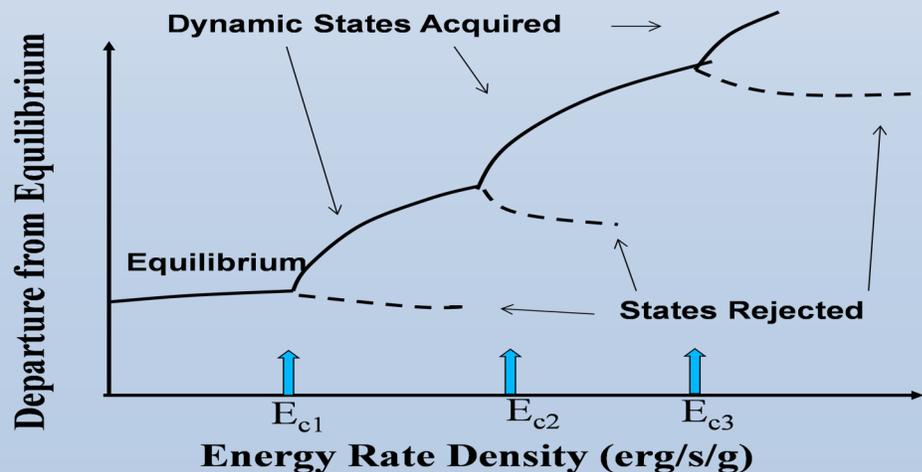
## Box 3: Self-Organization from Complexity

Peter Coveney, "Self-organization and complexity: a new age for theory, computation and experiment," Phil. Trans. R. Soc. Lond. A 361, 1057-1079 (2003). This paper describes self-organization as a property of far-from-equilibrium nonlinear dissipative dynamical systems. We quote from this paper:

" ……. *Complexity is the study of the behavior of large collections of such simple, interacting units, endowed with the potential to evolve with time. The complex phenomena that emerge from the dynamical behavior of these interacting units are referred to as self-organizing. More technically, my definition of self-organization is the spontaneous emergence of non-equilibrium structural organization on a macroscopic level, due to the collective interactions between a large numbers of (usually simple) microscopic objects. Such structural organization may be of a spatial, temporal or spatiotemporal nature, and is thus an emergent property…..*"
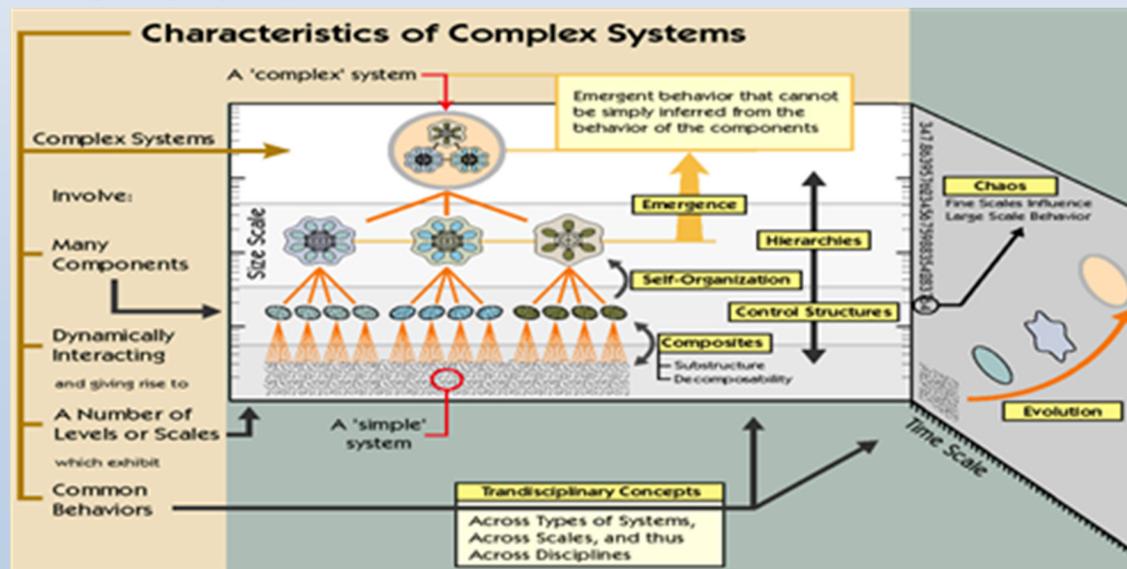


*Source: New England Complex Systems Institute, Cambridge*
*http://necsi.edu/projects/mclemens/cs_char.gif*

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# 2 The Characteristics of Hard X-rays to Probe the Evolution of Complexity

The title of this section defines the *technical driver* for the workshop. Hence, this section provides a preliminary perspective of the impact of hard x-rays on the science drivers, with a clear understanding that the workshop will define characteristics to address specific focus areas.

The synchrotron light source facilities provide electromagnetic radiation beams covering the infrared to hard x-ray regions. The use of these facilities has become indispensable to basic materials research given their ability to enable delineation of atomic-level understanding. In the context of the technical driver of this workshop, the discussion will focus *only* on hard x-ray sources. The techniques developed at both existing and future hard x-ray sources cover the spectroscopic and scattering methods that provide in-depth information on the behavior of atoms, electrons, and spins; information of hierarchical structures at multiple length scales from 0.1 nm to microns; and from surface monolayers to bulk. The time structure of the light sources has provided information on the temporal behavior of electrons, spins, and atoms in materials spanning the femtoseconds-to-seconds regions. Thus, in the past five decades, the U.S. Department of Energy (DOE) synchrotron hard x-ray sources have supplemented research in the *equilibrium sciences* by providing vital information on space and time correlations in materials sciences, nanosciences, chemical sciences, biosciences, and their engineering counter parts.

At the existing DOE facilities, the hard x-ray tools are used *with a primary emphasis to investigate equilibrium science.* They include the Advanced Photon Source (APS) at Argonne National Laboratory, the National Synchrotron Light Sources (NSLS I and II) at Brookhaven National Laboratory, and the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory. These facilities, with over 10,000 users during 2008 from the national labs, academia, and industries, form the core group of scientists and engineers to address the broad areas of research. A comprehensive survey and description of the U.S. light source facilities are well documented by DOE [1]. There are similar facilities in Europe and Asia. In particular, explicitly in support of hard x-ray research, European Synchrotron Radiation Facility (ESRF) in Grenoble, Positron-Electron Tandem Ring Accelerator III (PETRA III) in Hamburg, High Energy Accelerator Research Organization (KEK) in Tsukuba, and Super Photon Ring -8 (SPRing-8) in Hyogo must be mentioned (See www.lightsources.org).

The newcomer to the hard x-ray field is the free-electron self-amplified spontaneous emission (SASE) laser at LCLS that started early operations in October 2009 at SLAC National Accelerator Laboratory. In the future, the Euro-XFEL will join this rank, and the seeded x-ray FEL will provide superior transform-limited pulses allowing advances in the research areas discussed in this workshop.

As was emphasized in a recent DOE-sponsored workshop on Accelerator Enabled Discovery Science (Washington, D.C., Oct. 27-28, 2009) [2], no single light source can satisfy the diverse needs of the hard x-ray science community, and therefore, all technologies listed below that can advance non-equilibrium science will be included in the workshop discussion.

## 2.1  Compact Light Sources

New ideas have surfaced in the development of compact hard x-ray sources during the past 10 years, especially those that retain the advantageous characteristics of synchrotron radiation such as tunability and high monochromatic intensity. There are many approaches in realizing UV/hard x-rays using compact schemes:

*Mini Storage Rings*

*High-Harmonic Generation*

*Inverse Compton Sources*

*Plasma Sources*

*Plasma-Based Accelerator Sources*

A recent workshop on compact light sources (CS) reviewed the current developments in the field [3]. The conclusion was that every x-ray source has its important role as a light source. While high-brightness x-ray sources are the mainstay of today's research, such large-scale facilities have certain access limitations due to high user demand. Hence, compact sources will have a major role in the future when new ideas and technologies for their development are fully developed. High-harmonic generation (HHG), laser-driven plasma [4], and inverse Compton scattering sources [5,6] would represent an excellent alternative to large-scale facilities with promising properties. The electron accelerating capability of warm radio-frequency structures has extended their reach well past 100 MV/m, and new methods are being developed using direct laser acceleration (1 GeV/m), beam-driven dielectric wakefield acceleration (few GeV/m), and ultra-high-gradient laser- and electron-beam-driven plasma wakefield accelerators (>10 GeV/m). This offers the promise of future compact light sources, and a commensurately major impact on the cost of source construction.

These developments in CSs were discussed in the context of this workshop. Do these sources have suitable characteristics to support research in the areas of non-equilibrium science? What are the advantages, how can such sources be developed in the future to support *spatiotemporal measurements,* and what are the key experiments that CSs will support? Are compact sources suitable as pumps to impart energy (say in the THz/VUV wavelength range) to initiate a non-equilibrium process? Can such a source be used to seed hard x-ray cascade FELs?

## 2.2  Storage Rings

Storage rings remain the workhorse driving the majority of x-ray experiments. Beyond the remarkable impact made by the third-generation hard x-ray sources over the last two decades, and those expected from several major storage ring sources still coming online, we recognize the potential of storage ring technology to achieve the ultimate performance of *nearly* full transverse coherence in the hard x-ray range [7]. Future experiments at these sources will emphasize the *spatiotemporal domain* from

picoseconds to milliseconds, which is unique to these sources. The workshop participants identified key experiments that will influence the science drivers and define the hard x-ray characteristics that will allow such experiments to be performed.

## 2.3 Energy-Recovery Linacs

ERLs under development offer flexibility in terms of timing structure and high average brightness [8]. This linac-based transformational source allows superior performance over existing storage rings in terms of beam brightness and deliver linac-quality beam with a ~100-fs pulse width at very high (GHz) repetition rates. The needs of the science driver of this workshop with an ERL source to perform key experiments in a unique *spatiotemporal and transverse coherence domain* were discussed. The workshop participants proposed key experiments that can only be performed using ERL sources with specific hard x-ray characteristics.

## 2.4 X-ray FELs

The SASE XFELs are making an early impact in forefront science with their ability to deliver x-ray beams with full transverse coherence containing femtosecond pulses [9]. Some of the planned experiments will give a flavor of experiments to come in the non-equilibrium science areas of interest to this workshop. The workshop emphasized the exploitation of so-called seeded and self-seeded sources delivering transform-limited x-ray beams. Seeded and oscillator x-ray FELs offer fully controlled temporal coherence and intrinsic time stamping of the radiation in addition to the transverse coherence possible with SASE x-ray FELs. The phase-locked pulse train from future XFELs might lead to hard x-ray frequency comb capabilities. A class of key experiments proposed at this workshop will require *spatiotemporal control* at scales only available from XFEL sources. The large number of hard x-rays in a single pulse from such a source will be the key to investigating non-repetitive, non-equilibrium processes. A major workshop focus was on the specific characteristic of x-rays from XFELs [10] needed to meet the *spatiotemporal and full phase space coherence* requirements of the workshop science.

In Figure 2.1, a plot of the fractional unfiltered energy bandwidth from undulators at various sources is shown as a function of pulse width capabilities [10]. This represents only one of the key parameters of interest to the workshop science topics. More details are included in Reference [10].
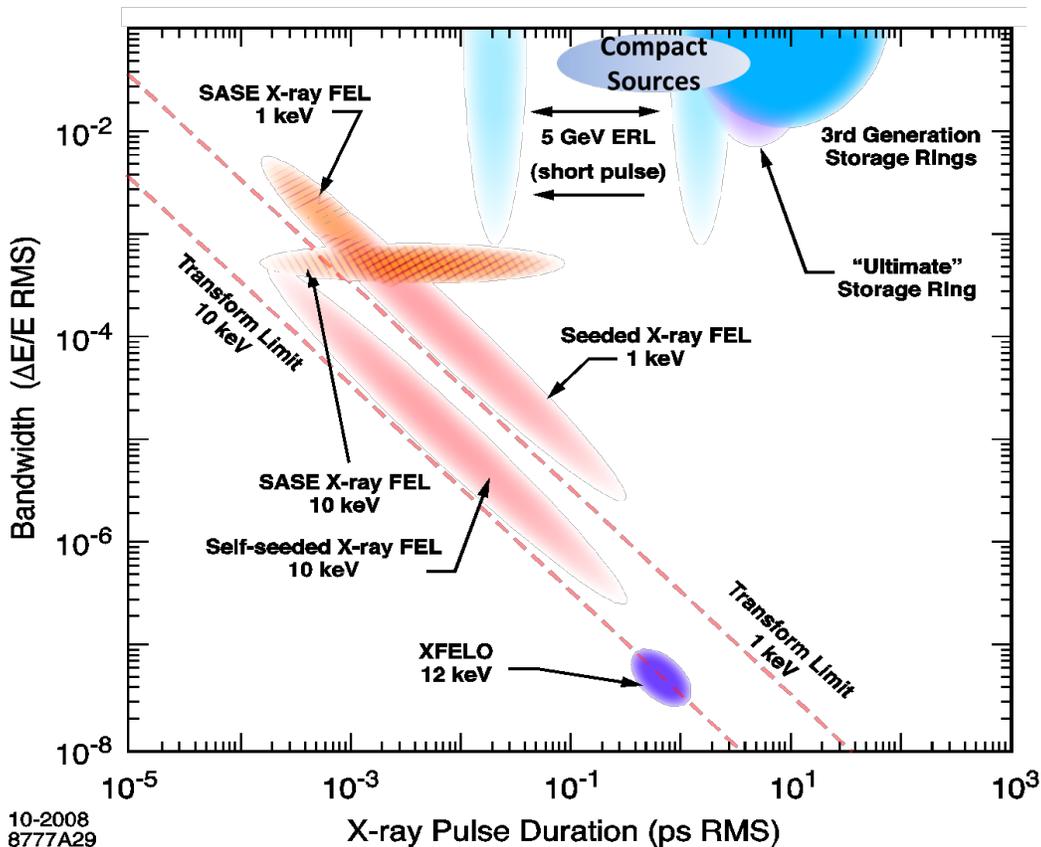
*Figure 2.1 Envelopes of unfiltered bandwidth from the undulators at various x-ray sources as a function of pulse width. The dashed lines indicate the transform limit at 1 keV and 10 keV [10].*

The workshop participants in each of the focus groups emphasized new science drivers in non-equilibrium science. It was apparent that there is a need to develop new approaches and tools for the study of the evolution of complexity using unique x-ray characteristics in the future (photon energy, controlled polarization, pulse-width, and degree of transverse and longitudinal coherence) [9]. The opportunity will be to explore the evolution of material complexity and coherent behavior at atomic-to-mesoscopic spatial scales and femtosecond-to-seconds of temporal scales. The biggest impact will be in understanding the evolution and knowledge to control complex material processes, such as those involved in energy conversion and storage. Some of the questions addressed at the workshop were:

- *What characteristics of advanced hard x-ray synchrotron light sources best fit the need?*

- *How does one synchronize the energy pumps — from which the nonlinear interactions are derived — with the probe pulse?*

- *What are the new techniques that should be developed for an effective use of the scatter-and-destroy strategy that will be prevalent in non-equilibrium studies, particularly of soft matter?*

In the following, we present a list of some of the parameters that were identified by the workshop to address key non-equilibrium science experiments.

- *High-average, low-peak brightness with high repetition rate (> MHz)*

- *High-peak brightness at lower repetition rate*

- *High peak power*

- *High transverse and longitudinal coherence*

- *Control of longitudinal phase space (including bunch length control from attoseconds to picoseconds – transform-limited x-ray pulse delivery)*

- *High photon energy resolution, tunability, and access to extended energies (~ 20 keV)*

- *Polarization control*

- *Phase-locked x-ray pulses (e.g., XFELO)*

- *X-ray sources for two- and multi-color wavelengths with time delays*

- *Control of x-ray pulse shapes*

- *Pump-probe synchronization to fs*

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[9] See for example, G. Geloni, E. Saldin, L. Samoylova, E. Schneidmiller, H. Sinn, Th. Tschentscher and M. Yurko, *Coherence properties of the European XFEL*, New J. Phys. 12, 035021 (2010); B. D. Patterson, R. Abela, H.-H. Braun, U. Flechsig, R. Ganter, Y. Kim, E. Kirk, A. Oppelt, M. Pedrozzi, S. Reiche, L. Rivkin, Th. Schmidt, B. Schmitt, V. N. Strocov, S. Tsujino and A. F. Wrulich, *Coherent science at the SwissFEL x-ray laser*, New J. Phys. 12, 035012 (2010)

[10] Uwe Bergmann, John Corlett, Steve Dierker, Roger Falcone, John Galayda, Murray Gibson, Jerry Hastings, Bob Hettel, John Hill, Zahid Hussain, Chi-Chang Kao, Janos Kirz, Gabrielle Long, Bill McCurdy, Tor Raubenheimer, Fernando Sannibale, John Seeman, Z.-X. Shen, Gopal Shenoy, Bob Schoenlein, Qun Shen, Brian Stephenson, Joachim Stöhr, and Alexander Zholents, Science and *Technology of Future Light Sources: A White Paper Report*, ANL-08/39, BNL-81895-2008, LBNL-1090E-2009, SLAC-R-917, December 2008: http://www.docstoc.com/docs/40759022/Science-and-Technology-of-Future-Light-Sources

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# 3  Focus Panels of the Workshop

The following six focus areas formed the core of the workshop discussions that identified science topics where the hard x-ray sources can contribute to the spatiotemporal knowledge.

***Focus Panel: Control of Complex Processes in Condensed Systems***

***Focus Panel: Controlling the Dynamics of Materials Processing***

***Focus Panel: Non-equilibrium Chemical Reactions***

***Focus Panel: Controlling Biological Functions***

***Focus Panel: Dynamics in Soft matter and Fluidics***

***Focus Panel: Nonlinear X-ray Science, X-ray Quantum Optics, and Extreme Metrology***

In addition to panel members, input was sought from technical specialists in source development, technique development, x-ray physics, x-ray optics, and instrumentation. The following detailed reports from each of these panels contain the major findings from this workshop.

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# 4  Focus Panel: Control of Complex Processes in Condensed Systems

| | | |
|---|---|---|
| *Panel Chair:* | *Sam Bader* | *Argonne National Laboratory* |
| *Cochairs:* | *Paul Evans* | *University of Wisconsin-Madison* |
| | *John Freeland* | *Argonne National Laboratory* |
| | | |
| *Participants:* | *Banerjee, Arnab* | *The University of Chicago* |
| | *Bertero, Gerardo* | *Western Digital Corporation* |
| | *Bianconi, Antonio* | *Sapienza Università di Roma* |
| | *Brock, Joel* | *Cornell University* |
| | *Choi, Byoung-Chul* | *University of Victoria* |
| | *Coppersmith, Susan* | *University of Wisconsin-Madison* |
| | *Dantus, Marcos* | *Michigan State University* |
| | *Dufresne, Eric* | *Argonne National Laboratory* |
| | *Durr, Hermann* | *SLAC National Accelerator Laboratory* |
| | *Evans, Paul* | *University of Wisconsin-Madison* |
| | *Freeland, John* | *Argonne National Laboratory* |
| | *Freelon, Byron* | *Lawrence Berkeley National Laboratory* |
| | *Ilavsky, Jan* | *Argonne National Laboratory* |
| | *Kevan, Stephen* | *University of Oregon* |
| | *Kimel, Alexey* | *Radboud University Nijmegen* |
| | *Kiskinova, Maya* | *Sincrotrone Trieste* |
| | *Lang, Jonathan* | *Argonne National Laboratory* |
| | *Lindau, Ingolf* | *SLAC National Accelerator Laboratory* |
| | *Lindenberg, Aaron* | *Stanford University* |
| | *Moncton, David* | *Massachusetts Institute of Technology* |
| | *Norman, Michael* | *Argonne National Laboratory* |
| | *Patterson, Bruce* | *Paul Scherrer Institute* |
| | *Ryan, Philip* | *Argonne National Laboratory* |
| | *Sarrao, John* | *Los Alamos National Laboratory* |
| | *Shen, Guoyin* | *Carnegie Institution of Washington* |
| | *Shenoy, Gopal* | *Argonne National Laboratory* |
| | *Shpyrko, Oleg* | *University of California, San Diego* |
| | *van Veenendaal, Michel* | *Argonne National Laboratory and Northern Illinois* |
| | *Viccaro, James* | *The University of Chicago* |
| | *Wen, Haidan* | *Argonne National Laboratory* |
| | *You, Hoydoo* | *Argonne National Laboratory* |
| | *Young, Linda* | *Argonne National Laboratory* |
| | *Zholents, Alexander* | *Argonne National Laboratory* |

## 4.1 Introduction

What is complexity in a condensed matter system? Condensed matter systems often possess a free-energy landscape that encompasses multiple energy, time, and length scales. Complexity occurs when the energy minima in the landscape are closely spaced due either to inhomogeneity or because the system has been driven into a far-from-equilibrium region of phase space. The properties and dynamics of the system depend on which local minimum is populated and both of the types of complex systems exhibit emergent phenomena arising from the complex energy landscape.

The most relevant minimum is difficult to identify. Because there are many competing minima their relative importance can be dynamically or systematically changed by small inputs. Small perturbations dramatically change the state of the system and lead to unexpected emergent properties, which are often distinct from the properties of the components of the system. Low-energy excitations have overriding importance in comprehensive descriptions of these systems.

The challenges posed in this focus panel of the workshop were to identify model systems, to uncover control strategies for complex condensed matter systems, and to propose a series of near-term investigations making use of new experimental techniques. Here we review the findings of the panel, which outlined many additional questions that could guide future developments in the field.

A large number of phenomena, from nanoscale electronic and magnetic dynamics [1-7] to photoinduced phase transitions [8-11], arise in complex systems driven far from equilibrium. Understanding and rationally controlling such systems is a scientific challenge that has been approached in materials science using non-equilibrium thermodynamics and transition state theory. The relevant processes and techniques in complex condensed matter systems with diverse magnetic and electronic and vibrational degrees of freedom are now being rapidly identified and probed (**see Box 1**).

It is a challenge to probe the pathways of the many degrees of freedom of complex condensed matter systems. The experimental techniques that are presently used to investigate equilibrium and near-equilibrium properties of materials often cannot be adapted to study these non-equilibrium states. For slowly evolving non-equilibrium systems, mean-field models and universal behavior provide some insights. To go beyond these methods requires the development of new experimental techniques to visualize the evolution of the system in both time and space [12-14].

After gathering input from a wide spectrum of participants, three open questions that define the field in complex condensed matter systems emerged:

- *How does an ordered system form out of a far-from-equilibrium state?*

- *How does the energy flow between different degrees of freedom?*

- *How can we measure the complex landscape of the free energy?*

This report presents selected case studies with respect to these questions.

## Box 1: Complexity of Mesoscale Fluctuations

While the atomic-scale, ultrafast-events often depend on 'simple' interactions and often follow simple rate laws, the evolution of complex dynamics at longer length scales still remains a mystery. Karine Chesnel, Joshua J. Turner, Mark Pfeifer, Stephen D. Kevan, "Probing complex materials with coherent soft x-rays," Appl. Phys. A 92, 431–437 (2008).

*"There are many physical, chemical, and biological systems that exhibit spatiotemporal hierarchies that lead to diverse, complex mesoscopic behaviors. For example, Å-scale chemical and physical interactions produce biopolymers that fold and assemble, often with astounding efficiency, into mesoscopic secondary, tertiary, and quaternary structures that support the diversity of macroscopic biological functions. Local interactions in glassy materials seem universally to produce unusual properties associated with tunneling centers which operate on the mesoscopic scale and which influence the macroscopic properties of glasses. Local exchange, hopping, and vibronic interactions in transition metal oxides and heavy Fermion conductors lead to a host of marginally ordered structures on the nanometer scale and sometimes to phase separation on a longer length scale, both of which help determine the unusual macroscopic properties of these materials....."*



*Masashi Kawasaki, Zhi-Xun Shen and colleagues recently demonstrated the phase separation in manganite films using magnetic impedance microscopy. The images on the right show the evolution of colossal magnetoresistance (@ 2.4T , 6.6T and 9.0T) through the growth of self-organized conducting filaments in a background of insulating phase. The filament direction and network was induced by disorder and strain in the film demonstrating the emergence of unique properties from mesoscopic interactions. Science 329, 190–193 (2010)*
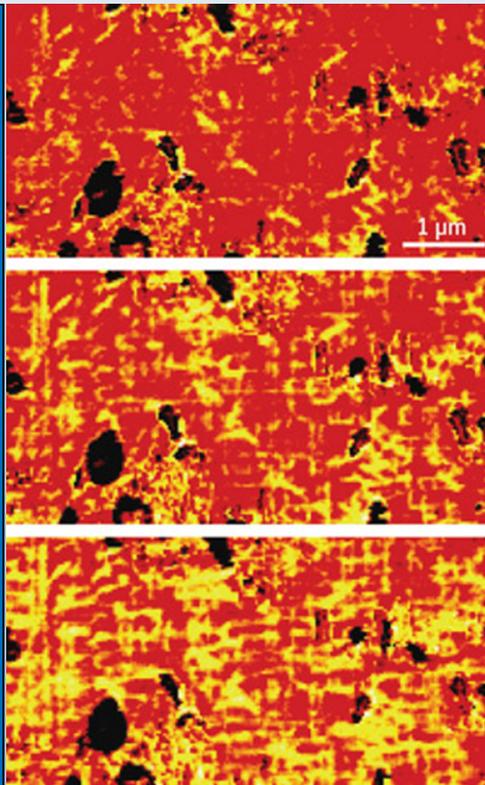
Two examples in magnetism arise from challenges in magnetic information technology: understanding non-equilibrium magnetization dynamics (Sec. 2), and the variation of the magnetic anisotropy during transient heating to the Curie temperature $T_C$ (Sec. 3). Correlated electron systems pose similar challenges, especially inhomogeneous states in complex oxides (Sec. 4). Control of complex materials properties can be achieved via photon-induced transitions (Sec. 5) or with ultrafast electric and magnetic field pulses (Sec. 6). Important challenges to theory arise in providing predictive descriptions of the dynamics of complex systems, from both statistical and first-principles perspectives (Sec. 7). The experiments required to make progress in understanding complex systems will benefit from new approaches including a variety of x-ray scattering and spectroscopy techniques based on new sources and new ways of exciting samples *in situ* during these studies (Sec. 8).

## 4.2 Non-Equilibrium Magnetization Dynamics

In nanomagnetic systems that are driven far from equilibrium, the presence of excess energy can lead to nucleation and growth of domains, propagation of short-wavelength spin-wave excitations, and the generation of magnetostatic modes [15]. The magnetic storage bit is driven far from equilibrium when the external field is switched much faster than the response time of the sample. Spatially resolved techniques are needed to observe the magnetic state of the material on the scale of the magnetic correlation lengths (10-20 nm). These correlations evolve in the femtosecond-to-nanosecond time regime. The development of related technologies, including integrated magnetic logic, magnetic random access memory, and spintronics also requires microscopy techniques with high resolution in both time and space. In hard-disk-drive (HDD) technology, advanced x-ray tools will enable measurement of the complex behavior that can point the way beyond Tbit/in$^2$ areal densities and Gbit/s data rates.

An example is the magnetization dynamics studied via the magneto-optical Kerr effect (MOKE) [16,17]. Magnetization maps obtained using time-resolved scanning MOKE microscopy with picosecond temporal resolution and submicron spatial resolution are shown in Figure 4.1. The switching process starts with the reversal of edge domains near the boundaries. A large number of nucleation sites or flux pinning centers then lead to complex structures. Simulations of the domain configuration show that the inclusion of thermally excited spin fluctuations creates stripe patterns, which differ from the irregularly shaped experimental patterns. The images in Figure 4.1(a)-(d) clearly show that the degree of complexity of the domain structure is a function of the speed of the switching. Fields with a shorter rise time induce switching via a more complicated domain pattern. Devices in which bits are manipulated on the picosecond time scale thus require a new level of understanding of the complexity of nanoscale magnets driven far from equilibrium.
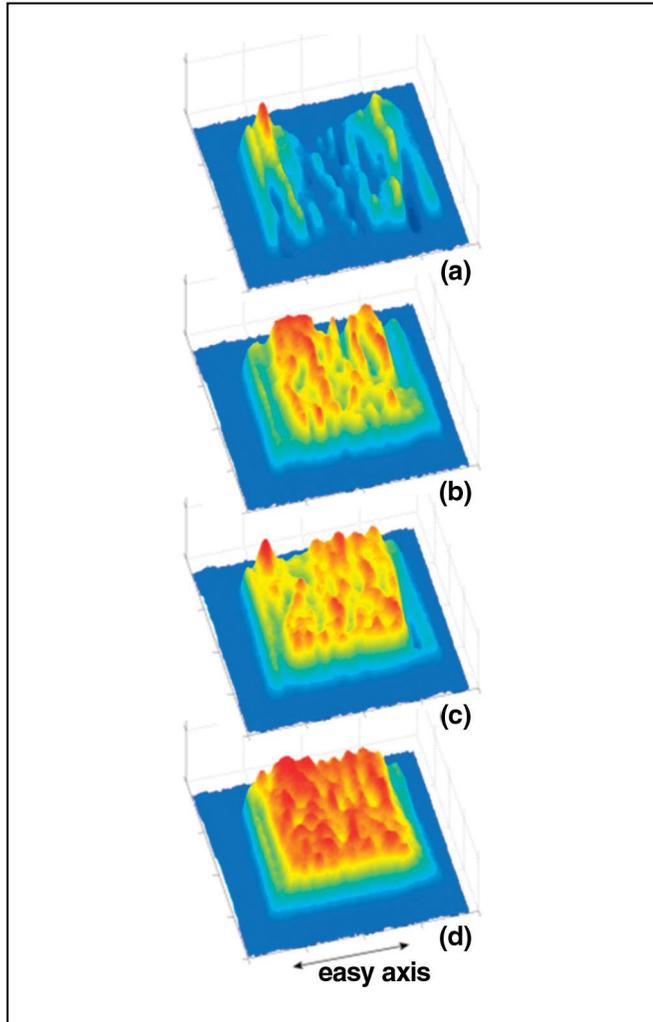
*Figure 4.1. Spatiotemporally resolved domain images representing the easy-axis magnetization component at selected time points after the onset of a magnetic switching field of 0.24 ns rise time (10%–90%). The 3D topography and color map both render the magnitude of the magnetic signal from unchanged (shown as white areas; blue in online version only) to fully reversed (shown as black areas; red in online version only)*

*(a) 750; (b) 800; (c) 850; and (d) 900 ps [17].*

A developing area of interest is in the transfer of spin angular momentum via the flow of pure spin currents created by magnetization dynamics in the absence of charge currents [18]. The transfer of spin angular momentum between ferromagnetic layers can be controlled by tuning the demagnetization dynamics or via femtosecond laser pulses. The capability to control magnetism directly with circularly-polarized light is rapidly emerging. This control requires both a sufficient photon flux to impart the required change in angular momentum in each optical pulse, and weak electron-electron scattering to allow the accumulation of angular momentum in the electron gas [19]. A demonstration of photon-helicity dependent demagnetization is shown in Figure 4.2 [19]. Here, the final state reached after the picosecond-scale optical transient depends on the helicity of the photon pulse.
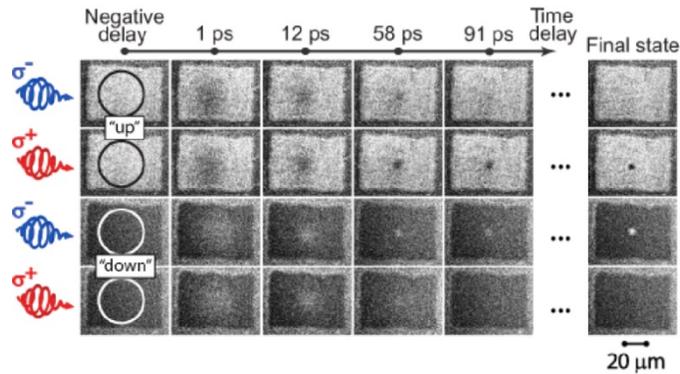
*Figure 4.2 Magnetization in $Gd_{24}Fe_{66:5}Co_{9:5}$ after excitation with $\square+$ and $\square$circularly polarized optical pulses. The domain is initially magnetized up (white) or down (black) and reaches final states shown in the right column. The circles indicate areas illuminated by the pump pulses [19].*

A key question that can be answered in studies with more precise probes is whether the spin and orbital moments in a ferromagnetic material respond in the same way to a strong perturbation. Answering this question provides insight into the nature of the spin-orbit interaction [20,21]. The dynamical changes initiated by laser-pump pulses in metals and alloys begin with the absorption of energy by electrons, triggering femtosecond-picosecond demagnetization, followed by recovery of magnetization over hundreds of picosecond. If the pump laser intensity drives the system into a regime in which its response is nonlinear, it is possible to demagnetize the sample or to switch the magnetization via proper choice of the chirality and intensity of the pump beam. This effect has been demonstrated in ferromagnetic CoPd thin films excited by a near-infrared femtosecond laser. The magnetic response of the orbital and the spin magnetic moments was probed using femtosecond-resolved x-ray magnetic circular dichroism at the $L_2$ and $L_3$ absorption edges of Co [20]. Analysis of the dynamics enabled the separation of the contributions of the projected orbital and spin moments. The magneto-crystalline anisotropy energy also plays an important role in the reduction of the total magnetization observed far from equilibrium. The future lies in more fully understanding the mechanisms involved in ultrafast, nonlinear processes, and in turn, using the new insights to improve magnetic information storage devices **(See Box 2).**

Although photo-excited magnetic transients have been reported in a large class of systems. e.g., as in Fig. 4.2 and [22], the underlying non-equilibrium evolution of the order has yet to be completely understood. Key experiments in the complexity of magnetic systems will address the following:

- *How is switching controlled via application of photonic fields? Can spin ordering be controlled by femtosecond x-ray pulses?*

- *What new opportunities arise from photon helicity switching of spin angular momentum?*

- *How does one control the magnetization in order to proceed through selected excitation channels?*

# Box 2: Femtosecond Magnetism

Excitation of magnetic materials by intense femtosecond laser pulses develops strong non-equilibrium conditions in the electron and spin systems that has both fundamental and applied consequences, and leads to many new questions. Can light manipulate and control the magnetization? What are the ultimate limits on size and speed of magnetic switching? How to understand sub-100-ps magnetization dynamics at a sub-100-nm scale? What is the mechanism for the energy transfer from the light to the magnetic system? How do photons interact with charges, spins, and lattice, and how does the angular momentum transfer between them? How fast and between which reservoirs can angular momentum be exchanged and is this even possible on time scales shorter than that of the spin-orbit interaction? What theoretical tools are needed to handle strong quantum mechanical nature of the electrons and spins, potentially exhibit tunneling, interference, entanglement, and large coherence effects?

These questions are addressed in detail realizing that the ultrafast magnetization dynamics is connected to the changes in a magnetic system as energy and angular momentum are exchanged between the thermodynamic reservoirs of the system (see the figure).

Time scales in magnetism from various interactions. The short duration of the laser pulses makes them an attractive alternative to manipulate the magnetization.
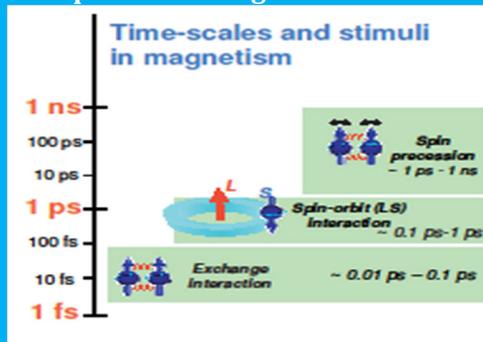
Stimulated coherent Raman scattering, a possible microscopic mechanism responsible for an ultrafast optically generated magnetic field.
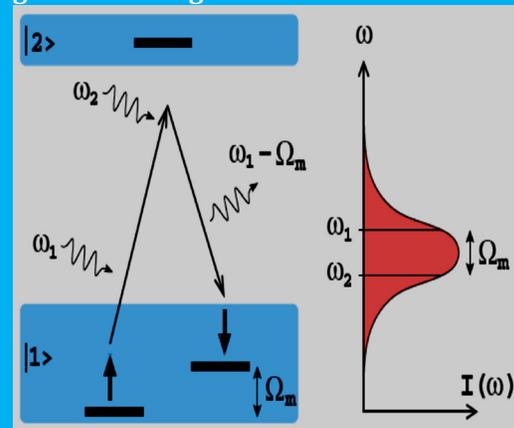


The stimulated coherent Raman scattering is a likely microscopic mechanism responsible for an optically generated femtosecond magnetic field. As shown in the figure (right), two frequency components of the electromagnetic radiation from the spectrally broad laser pulse take part in the process. The frequency $\omega_1$ causes a transition into a virtual state with strong spin-orbit coupling. Radiation at the frequency $\omega_2$ stimulates the relaxation back to the ground state together with the creation of a femtosecond magnon of energy $\Omega_m$. For details: Andrei Kirilyuk, Alexey V. Kimel, and Theo Rasing, *Ultrafast optical manipulation of magnetic order*, Rev. Mod. Phys. 82, 2744 – 2784 (2010); Bruce D Patterson, *Resource Letter on Stimulated Inelastic x-ray Scattering at an XFEL,* SLAC Technical Note: SLAC-TN-10-026 (2010).

- *How is the demagnetization of domain structures nucleated during the far-from-equilibrium excitation?*

- *How can the nucleation process be imaged with the necessary time, space, and chemical resolution in a single-shot femtosecond x-ray experiment?*

- *What are the nonlinear physical mechanisms involved in inducing femtosecond magnetism with light and how do we unravel them?*

- *What are the ultimate limits of the speed of magnetic switching?*

Improving the space- and time-resolution of x-ray techniques can dramatically advance the field. It is especially important to couple these capabilities to in situ investigations. For example, imaging the spin structure in a single microstate of the system and following its development would have great value. A crucial experimental development in this sense will be a sample environment in which a large switching field (~1 T) can be applied with picosecond rise time in order to study high-anisotropy materials [23].

## 4.3 Experimental Determination of Anisotropy Fluctuations near the Curie Temperature

Magnetic HDD technology continues to address the growing demand for massive storage of information. HDD technology has a small-bit cell and high areal density relative to other information storage media. The HDD industry recently transitioned from longitudinal to perpendicular magnetic recording. However, perpendicular recording can only support a limited number of product generations before facing physical limits. Innovative advances can extend the technology to higher densities likely to surpass the $Tb/in^2$ mark. These advances include energy-assisted magnetic recording and bit-patterned media.
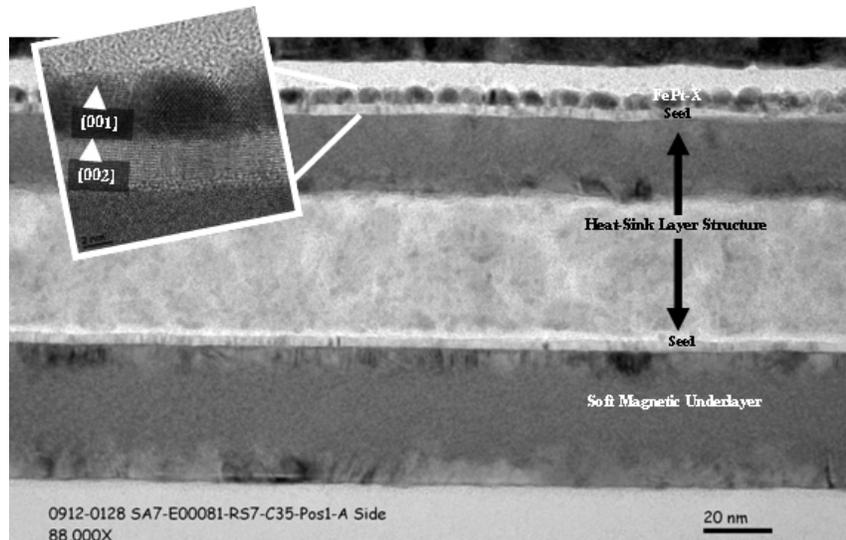


*Figure 4.3  Experimental heat-assisted magnetic recording media incorporating a heat-sink structure and high magnetic anisotropy, atomically ordered L10 FePt storage layer. The grain size for the storage layer needs to be 4.5 nm or smaller. Magnetic anisotropy near $T_C$ is not yet well understood (Figure provided by Gerardo Bertero Western Digital).*

One likely enabling technology is heat-assisted magnetic recording. The promise of heat-assisted recording is rooted on the premise of extremely high effective head-field gradients resulting from the combination of large temperature and magnetic field gradients. These effective field gradients can be an order-of-magnitude larger than those possible with purely magnetic fields. Heat-assisted recording uses a laser source with a beam diameter of hundreds of nanometers to heat a magnetic bit of similar length scale. The bit is heated to close to the magnetic Curie temperature $T_C$, thus reducing its coercivity at the instant of writing. In order to capitalize on the high switching gradients and achieve high recording density, the magnetic anisotropy must be high and the $T_C$ value must be low, although higher than room temperature. The ordered $L1_0$ FePt intermetallic compound (Fig. 4.3) is a nearly ideal material in this respect, satisfying both of the conditions.

At present, the design of heat-assisted recording materials is based on estimates of the *effective* head-field gradients, which incorporate magnetic and thermal gradients and magnetic anisotropy distributions in the media. These estimates are, however, based on equilibrium measurements of the temperature variation of the magnetic anisotropy. It is not at all clear that the non-equilibrium state induced by the optical radiation is accurately described by these assumptions. Preliminary modeling results indicate that in small-grain media, phonon-magnon interactions can lead to large fluctuations in anisotropy ($H_k$) near $T_C$ (Fig. 4.4) and that these fluctuations can limit the resolution of the writing process [24]. If experiments confirm this behavior, ways to minimize the negative effects will be needed.
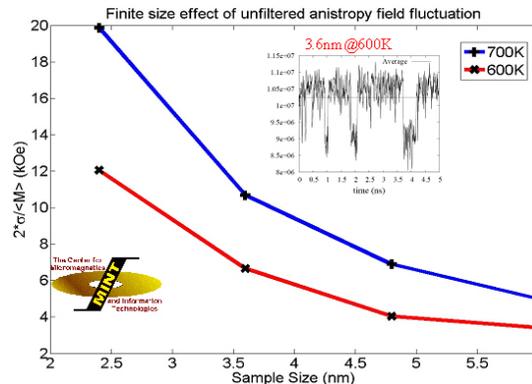


*Figure 4.4 Variation of the anisotropy field as a function of sample size. At elevated temperature, spins in the magnetic grain will fluctuate wildly, both reducing the anisotropy and causing it to fluctuate. This effect is only partly captured by the concept of superparamagnetism. The fluctuations lead to jitter during magnetic recording. Heat-assisted magnetic recording is on a sub-nanoosecond scale. The fluctuation of the anisotropy can have significant impact on the writing process. Experiments with picosecond-scale resolution are required to capture these fluctuations. (Figure provided by R. Victora, Univ. of Minnesota).*

Modeling is presently incomplete because the dynamic variation of the magnetization is a new issue that has not been addressed adequately in the past. Furthermore, experimental measurements of the fluctuations in $H_k$ near $T_C$ in nanoscale granular samples are not yet available. These experiments will be enabled by new advances in light-source facilities, and would have an important impact on the development of HDD technology. Time-resolved measurements of the magnetic anisotropy with sub-

nanosecond resolution are needed in order to detect the anisotropy fluctuations. Increased attention is being invested in this critical topic by the HDD industry, which is now in the process of forming an industry-wide consortium to address problems of this nature.

In addition to the design and technology issues that must be addressed in order to develop improved HDD technologies, there are equally important non-equilibrium physics problems in the nanometer length scale and picosecond temporal scale. These include:

- *The spin orientation and its reproducibility near $T_C$.*
- *The response of the spin structure to applied switching field and damping forces.*
- *The dynamics of magnetic domains following the picosecond heat pulse.*
- *The coupling of spins to adjacent recording grains.*
- *The identification of optimized interfacial structures for efficient high-speed heat transfer to the adjoining heat-sink layer.*
- *Probing structural changes arising from repeated heating and cooling cycles of magnetic nanostructures.*

## 4.4  Correlated Electron Systems Far from Equilibrium

Correlated electron systems are inherently highly nonlinear, such that the choice of ground state is dictated by a subtle balance between the energetics of multiple degrees of freedom. The ground states of complex oxides often exist in a free-energy landscape with multiple competing local minima, and are thus similar to non-equilibrium states that evolve in space and time when a system is driven far from equilibrium. In both cases, there are a large number of states with similar energies but vastly different properties. Driving complex oxides far from equilibrium, thus, does not require pumps delivering large energy, making their use in applications quite attractive. Confinement effects caused by surface modifications, interfacial proximity effects with different materials, defects, and externally induced perturbations can shift the delicate balance between competing interactions and vastly alter the ground state. In colossal magneto-resistive (CMR) materials, for example, a change in resistivity of nearly 10 orders of magnitude is realized by applying a modest magnetic field. A non-equilibrium state is reached via a stimulus that provides a pathway to a specific minimum in the energy landscape.

Transition-metal oxides are of interest because they possess electronic and magnetic phenomena that originate from strong correlations [25]. New states can be created in these complex oxides using a variety of stimuli, including magnetic or electric impulses, dynamic variations in stress or hydrostatic pressure, and optical or x-ray excitation. The relevant physical phenomena are incredibly diverse: electron transport [26], metal-to-insulator transitions [27], persistent or transient superconducting order [28, 29], magnetic order [30], and molecular order in charge transfer compounds [31, 32].

The following questions were posed for discussion within the panel with respect to hard x-techniques.

- *How does the non-homogeneous distribution of magnetic, electronic, or structural order parameters evolve as the non-equilibrium state returns to equilibrium?*

- *To what extent is the non-equilibriums state reproducible? Does one realize the same nanoscale state each time the system is driven out of equilibrium?*

- *Will such experiments address the theoretical understanding of photo-excitation phenomena [33]?*

In large part, the complexity of transition metal oxides arises from both intrinsic and extrinsic phase separation on diverse length scales [34]. Understanding phase separation presents a significant opportunity in unraveling the intrinsic physics of these systems. Many of the most useful techniques in condensed matter physics, however, lack the spatial resolution needed to explore the phase separation at the relevant length scales. Thus, it is imperative to develop new experimental approaches. In part this need can be addressed using two recent developments in x-ray focusing and coherent scattering.

X-ray focusing optics allows x-ray microscopy to be performed in either full-field imaging or scanning diffraction modes. Recent advances in x-ray focusing enable microscopy maps of structural, electronic, and magnetic properties of materials with spatial resolution of 10s of nanometers, as illustrated in Fig. 4.5 [35].

The increase in spectral brightness and coherent properties of x-ray beams of new-generation light sources enables lens-less imaging approaches, where the objective optic is replaced by phase-retrieval algorithms [36-39]. A high degree of transverse phase coherence of the x-ray beams is already provided by third-generation synchrotron sources and x-ray free-electron laser facilities. The coherence will be a defining characteristic of experiments at sources that are either being constructed or proposed, including soft- and hard-x-ray free-electron lasers and at energy recovery linear accelerators. Phase coherence in the x-ray beams from these sources makes it possible to combine nanofocused x-ray beams with coherent scattering techniques, including coherent diffractive imaging [38-42]
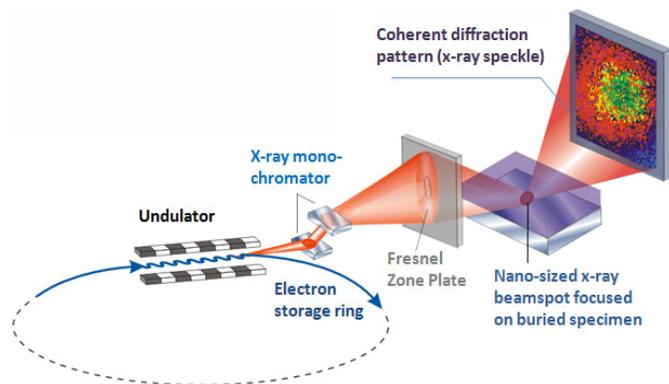


*Figure 4.5  x-ray nanoprobe imaging and coherent scattering.*

With this approach, ptychography [43,44] and scanning x-ray diffraction microscopy [45], for example, can be used to image extended objects with spatial resolution that is several times smaller than the illuminated volume. Order-of-magnitude improvement from the present 5-20-nm resolution is expected over the next decade as new types of light sources and optical elements become available.

## 4.5  Light-Induced Phase Transitions in Complex Materials

Optical excitation provides the means to drive complex systems into far-from-equilibrium states. Ultrafast optical sources, for example, can produce large and easily varied concentrations of electron-hole pairs without changing the composition of the material, thus avoiding the inherent difficulties of controlling stoichiometry, uniformity, and homogeneity. Continuous photo-excitation of cuprate superconductors and magnetic manganites at fixed temperature can yield large changes observed in the conductivity, Hall effect, mobility, and superconducting transition temperature.

Optical excitation enables materials with new properties to be created in a controlled fashion. Achieving this control leads, in turn, to a series of fundamental questions **(see Box 3)**. For example, if photo-doping yields a superconducting phase [28, 29] what are the differences between that state and the superconducting phase reached by chemical doping?  Gedik *et al*. acquired ultrafast electron-diffraction structural information during the photo-doping of antiferromagnetic YBaCaCuO with 1.55-eV photons and argued that the observed structural changes are the signature of the superconducting phase [46, 47].
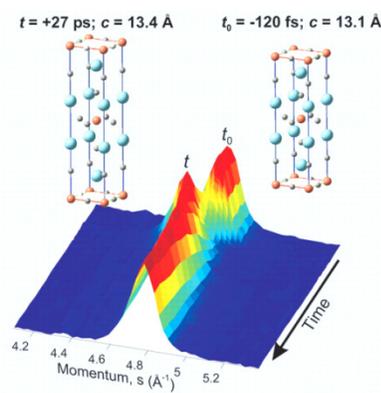


*Figure 4.6  Evolution of the cuprate crystal structure after optical excitation [47].*

Transitioning into the time domain will provide a better picture of how these properties evolve and of the fundamental microscopic changes underlying them.

This phase is thought to be induced by a *p*-to-*d* charge transfer from oxygen ($O^{2-}$) to copper ($Cu^{2+}$) in the Cu-O *ab*-planes, resulting in a tetragonal expansion of the lattice, as in Fig. 4.6. Gedik *et al*. also note that the threshold for this transition is ~0.12 photons per copper site, which is close to the

concentration per Cu site of chemically doped carriers required to induce superconductivity in this oxide.

Large photon fluxes can also induce metal-insulator transitions. In $VO_2$, a prototypical compound exhibiting a metal-insulator transition, Cavalleri *et al.* monitored dynamical changes in the structure using diffraction [48] and in the electronic structure using time-resolved oxygen-edge spectroscopy [49]. Similar studies have also followed the metal-insulator transition in $PrCaMnO_3$ (PCMO) under dynamic excitation. PCMO is particularly interesting because there is no metallic phase in the ground-state phase diagram, and the metallic phase must thus be produced by external excitations [50, 51]  Advanced experimental techniques can provide further microscopic detail, for example observing the evolution of the Fermi surface during the dynamic melting of the charge density wave state in $TbTe_3$ [52].

Optical pumping with visible photons, however, also simultaneously excites many other degrees of freedom, including excitations of substitutional dopants and thermal vibrations. Unravelling these excitations can be quite difficult, and it can be advantageous to use excitations that couple more specifically to individual physical processes. Recently, for example, it was shown that an insulator-metal transition can be driven in PCMO when a Mn-O stretching vibration is selectively excited with mid-infrared radiation [53]. Such an excitation enables one to directly trigger phase changes via a well-defined path. This provides insight into the mechanism that generates the dynamic phase transition. For example, in the case of PCMO, the key was to directly alter the local energy via a dynamic distortion that affects the crystal field energy.

Exciting a specific vibrational mode similarly provides large changes in the properties of high-temperature cuprate superconductors, where one-dimensional (1-D) stripes, spin- and charge-order, and superconductivity are closely related. One such stripe-ordered compound, non-superconducting $La_{1.675}Eu_{0.2}Sr_{0.125}CuO_4$, is transformed into a transient three-dimensional (3-D) superconductor after excitation using mid-infrared femtosecond optical pulses, as shown in Fig. 4.7. The emergence of coherent interlayer transport is signalled by the prompt appearance of a Josephson plasma resonance in the *c*-axis optical properties. An upper limit for the time scale needed to form the superconducting phase is estimated to be 1-2 ps, significantly faster than expected. Time-resolved experiments provide new insight into the competition of electronic phases in the cuprates, and a strategy that can be extended to other complex systems.

The ability to introduce phase transitions using optical techniques leads to a series of fundamental questions that can be addressed experimentally:

- *Does the effect cooperatively manifest itself at the nanoscale (e.g., via forming nanodomains of superconducting order)?*
- *How do we measure the photoinduced superconducting properties of a nanodomain in real time?*
- *Can we predict photo-initiated new and interesting functionalities in correlated electron systems from theory?*
- *Can we realize a photoinduced transient superconducting state in manganites?*

- *Can we use some of the exotic nanoscale excitations, like orbital or plasmon excitations of complex matter, to transfer information over nanoscale lengths?*

- *What other opportunities are there in the use of coherently shaping the acoustic phonons [54]?*

- *What are the problems in condensed matter where coherent control is important [55]?*
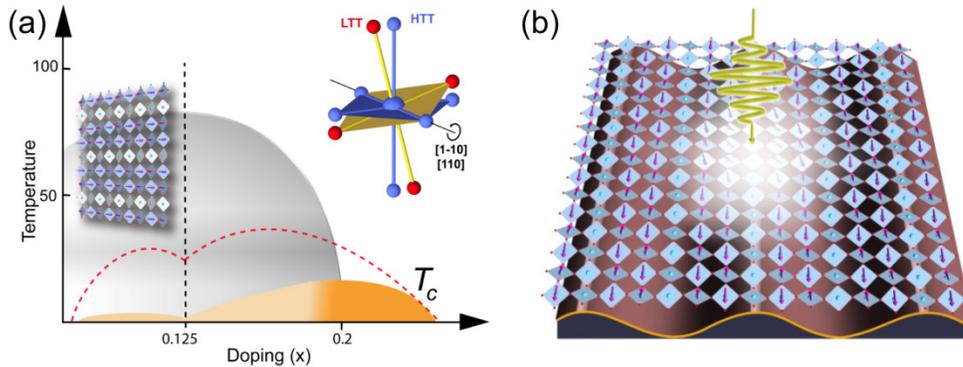


Figure 4.7 (a) Phase diagram of the $LaEuSrCuO_4$ system with equilibrium stripe-ordered (gray) and superconducting phases (gold). (b) A transformation from the stripe-ordered phase to the superconducting phase can be induced by optical absorption [56].

## 4.6 Ultrafast Electric/Magnetic Field Pumps

The state of complex materials can be altered by large applied electric or magnetic fields. In semiconductors, for example, varying the concentration of charge carriers using a gate electric field can induce a metal-insulator transition, or it can scan the Fermi level through a series of quantized two-dimensional (2-D) ground states [57]. Field-driven effects can similarly lead to magnetic or structural phase transitions or produce states that are not available in equilibrium systems of the same composition [57]. The range of relevant electric fields and carrier concentrations extends across several orders of magnitude, as shown in Fig. 4.8. The dynamics of the electrostatic-field-induced transitions can involve the nucleation and growth of new phases as the energy landscape is rapidly altered. A second strategy is applicable to insulators, where it has been predicted that the phase of a material can be selected by placing it in a large electric field [58]. In systems with magnetic moments, large magnetic fields can drive phase transitions in other order parameters, as in the magnetic manipulation of the stored electrical polarization in magnetic multiferroics [59]. In both the carrier-induced and electrostatic cases, the ease and speed of controlling the complex systems under investigation makes experiments particularly precise and scientifically valuable.

## Box 3: A Search for Photoinduced Hidden Dynamic States

Recently it has been demonstrated that the spontaneous emergence of orders in the transition metal oxides, involving complex combinations of charge-, spin-, and orbital states, can easily be induced or controlled by the application of THz or optical laser fields. For example, one may drive a system between Ohmic (resistive) and superconducting states or induce ultrafast melting of antiferromagnetic order. These hidden emergent orders in materials cannot be reached by the conventional thermal processes or through the application of large pressures, and electric or magnetic fields. Thermally driven order follows equilibrium thermodynamics while the photoinduced hidden order of a system manifest through a cooperative interaction through the excited states of the system. The hidden phases are characterized from dynamic spectroscopic measurements which probe the electronic changes caused by transient states, and from time domain diffraction measurements that measure the transient changes in the structural order.

An illustrative example is $Nd_{0.5}Sr_{0.5}MnO_3$ (NSMO) film deposited on SRO. The film exhibits a first-order orbital-ordered (OO) and insulator–metal (IM) transition at $T_{IM}$=180 K. This thermally induced so-called M phase with nearly an isotropic structure is realized from an insulating charge- and oribital-ordered (CO-OO) ground state with a structure that is expanded along the b axis and contracted along the c axis. But when the system is excited by a laser-pulse, a photoinduced hidden phase is realized with unique Jahn-Teller distortions in the orbital state shown in the figure below (see expanded blue and green orbital lobes). The photoinduced phase is homogeneous and is realized soon after the film is photoexcited and lasts for at least a few ns.
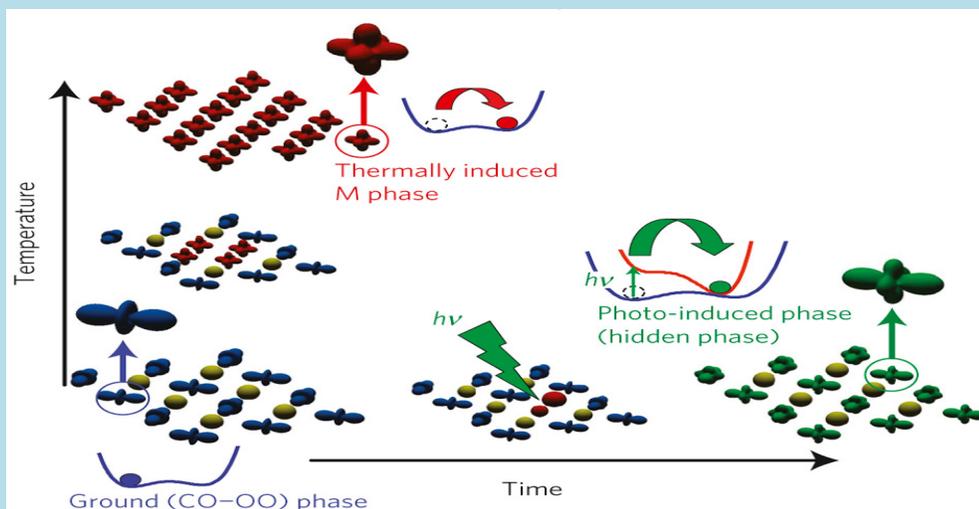


*Schematic illustration contrasting the orbital character of a photoinduced hidden phase with that of a thermally induced M phase converted from the initial CO–OO state (ground state).* (Hirohiko Ichikawa, et al., *Transient photoinduced 'hidden' phase in a manganite*, Nature Materials 10, 101-105, 2011).

The critical challenge in understanding field-driven phase transitions is to develop characterization tools that enable structural, electronic, and magnetic effects to be probed *in situ*. The modification of materials using applied electric fields extends to complex oxides, colossal magnetoresistance materials, organic semiconductors, piezoelectrics, ferroelectrics and multiferroics, and charge-density wave materials, and results in structural, magnetic, and electronic changes. The route that these materials take through the transition driven by the applied fields can be probed with new time-resolved x-ray techniques. These experiments will yield an understanding of the changes in local chemical state, strain patterns with atomic and nanoscopic resolution, and atomic order within nanoscopic domains during phase changes, and associated with the local ferroelectric polarization. Coherent imaging capabilities, microscopy, and ultrafast scattering techniques, in addition to conventional spectroscopies and monochromatic- and polychromatic-diffraction techniques, provide crucial insights.

The time response of the properties following the electric-field modification is critical in controlling these properties. Domain dynamics, the temporal development of strain, and the coupling of applied fields to acoustic phonons are intrinsically non-linear and time dependent and must be imaged at their fundamental time and length scales. The relevant phenomena have characteristic times ranging from femtosecond to nanosecond.

The manipulation of the ferroelectric polarization, for example, includes a switching process mediated by domains, as has been studied at varying length scales since the 1950s. Recently, however, a class of ferroelectric superlattices was identified in which the polarization spontaneously decomposes into striped nanodomains [60]. The dynamics of these domains occurs on nanosecond timescales and sub-10-nm length scales. Recent studies have shown that the long [60] and short [61] time-scale dynamics of these nanoscale features can be probed via diffraction. These studies, however, still provide only an average statistical insight into the dynamics because they lack sufficient spatial resolution. Vast opportunities remain for ultrafast nanometer-scale imaging.

Large fields also lead to non-linear responses that are only beginning to be understood. The study of nonlinear behavior can be extended using structural tools that allow the state of the materials to be probed in very large transient fields, as has recently been demonstrated in $Pb(Zr,Ti)O_3$ thin films [62]. In other materials, it is predicted that new emergent states with ferroelectric or other unique cooperative properties can be nucleated if the system is driven into the nonlinear regime with large fields. Increasing the magnitude of the applied fields and decreasing the duration for which they are applied will allow us to gather new information on the temporal behavior of emergent states, as well as on the cooperative aspects of the transition and its dependence on the pinning centers, such as impurities, strains, and other inhomogeneities. This type of experiment will resolve the mechanism of magnetization switching of a ferromagnet using electric fields, proposed recently [63], and whether it is possible to drive the magnetic system into a non-equilibrium state beyond that described by Landau-Lifshitz-Gilbert theory.
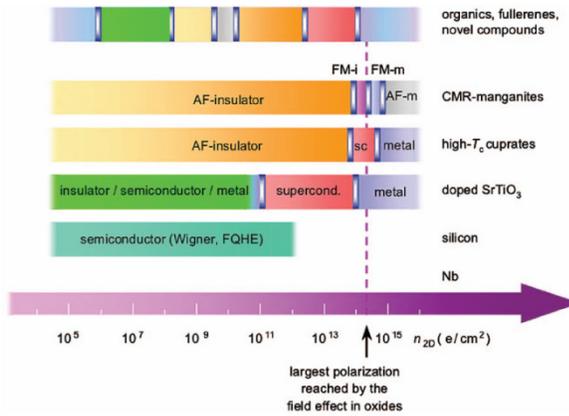
*Figure 4.8* Phases of 2-D correlated materials as a function of sheet charge density. Silicon is shown as a reference. The examples for high-temperature superconductors and for colossal magnetoresistive manganites reflect $YBa_2Cu_3O_7$ and La,SrMnO$_3$, respectively. The top bar shows schematically the richness of materials available for field-effect tuning and the spectrum of their phases. AF, FM, I, M, SC, FQHE, and Wigner stand for antiferromagnetic, ferromagnetic, insulator, metal, superconductor, fractional quantum Hall effect, and Wigner crystal, respectively [57].

An exciting opportunity to perform exploratory experiments is to use a ballistic electric field from a high-energy (10-25-GeV) electron pulse from a linear accelerator with 100-fs width (*e.g.,* at SLAC or Hamburg). The field would be applied to a suitable thin film of ferroelectric material and monitored in the time domain by hard x-ray imaging tools to follow the evolution of new phases, structures, and polarization states over the entire sample. The generated electric field can be as high as many volts per nanometer, which should be adequate to drive oxide systems into the nonlinear regime. Alternatively, large fields can be generated using single-cycle THz pulses produced using ultrafast techniques.

## 4.7 Theory of Non-Equilibrium Condensed Matter

Condensed matter theory faces challenges in predicting the behavior of nanoscale systems far from equilibrium. In deterministic systems driven far from equilibrium, where nonlinearities are important, theoretical progress has been limited to simple situations. Examples include the onset of symmetry breaking, the stability of perfect patterns, and the motions of single topological defects in otherwise perfect patterns. Theorists have not yet developed an understanding of disordered arrays of defects, patches of uncorrelated regions, and chaotic or ordered dynamics [64, 65] in maroscopic, deterministic, far-from-equilibrium systems. Macroscopic features may be amenable to mesoscopic theory, such as to describe locally ordered stripe or hexagonal patterns, and dislocation, spiral, and target defects. This can be accomplished by a combined molecular-dynamics and Monte Carlo approach to describe atom and carrier dynamics, respectively, and to investigate the thermodynamic evolution of the system during heating, expansion, and cooling [66, 67].

The systems can also display striking microscopic behavior, such as dramatic changes in symmetry to modifications of experimental parameters. The thermodynamic pathways through transformational dynamics must also be investigated using modern tools of computational science. A fully quantum-mechanical treatment is challenging, but efforts to provide such a treatment are beginning [68].

## 4.8  Opportunities/Needs

The experiments described by the participants in the 2010 Complexity Workshop require developments both in sources of excitation and in probes of the properties of materials. With respect to excitation sources, we have emphasized the use of ultrafast optical pulses to drive the system far from equilibrium. There are, however, a variety of relevant sources that will provide rich experimental opportunities. For example, one might use:

- *FEL pulses from a fourth-generation source (in a two-color- or two-undulator-source experiment).*
- *Relativistic electron bunches from an accelerator that can generate large electric and magnetic fields with picosecond-to-femtosecond pulse width.*
- *THz pulses generated at an accelerator, or using new laser methods to stimulate vibrational properties in a controlled fashion.*
- *Optimized GHz device structures providing transient electric and magnetic fields.*

With respect to the development of new probes for complex systems, it is clear that specific methods for probing non-equilibrium properties with *simultaneously* high spatial and temporal resolution are urgently needed. These can include coherent scattering and microscopy at existing storage-ring-based light sources, and at upgraded versions of these sources. In addition, the development of emerging sources, including free-electron lasers, provides the means to increase by orders of magnitude the sensitivity and temporal resolution of these techniques. In both cases, the sources must be coupled to novel excitation methods and must provide versatile sample environments to reach their full potential in complex condensed matter systems.

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# 5 Focus Panel: Controlling the Dynamics of Materials Processing

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## 5.1 Introduction

Virtually all useful materials and processes involve non-equilibrium states, either as intermediaries on the route to a final product or for the final product itself. This is at the core of materials science and has been the basis of manufacturing processes used in all industrial materials. For example, microstructure modification and the controlled introduction of defects in the materials by rolling, extrusion, alloying, solute precipitation, and thermal cycling are key processes in the manufacture of metallic alloys. Traditionally, materials processing involves conditions close to equilibrium, but processing far from equilibrium provides new opportunities for creating materials with novel properties. In both cases, a better understanding of the dynamics of the underlying physical mechanisms holds the potential for improved efficiency and achieving desired properties. By all measures, industry has been phenomenally successful in the (top-down) development and refinement of new materials and materials processing steps that form the basis of all present materials processing technologies. However, often missing are systematic (bottom-up) approaches based on fundamental understanding of the physical properties of materials, materials microstructure, and materials processing steps that are needed for the development materials and materials properties outside known envelopes.

The natural complexity of materials microstructure under processing and the lack of experimental probes of internal structure have prevented comprehensive characterization of defect structures *as they are formed*. There are several origins of complexity in materials processing. The first is the complexity of the structure of the material itself, and in particular, its microstructure. The structure of a single crystal can be simply described in terms of a lattice and atomic basis, and the structure of an amorphous solid or liquid can be described in terms of short-range atomic order. But there are no similarly simple descriptors for polycrystalline or multiphase materials. For example, specifying the relative orientation of just two grains, together with a planar boundary between them, requires five variables—and most practical materials have vast numbers of grains.

A related issue is heterogeneity. Any material more complicated than a defect-free single crystal is heterogeneous on some length scale, and many materials are heterogeneous on several length scales. Interfaces constitute a critical heterogeneity in polycrystalline materials, and the interplay of grain boundaries with defects largely governs overall behavior. The ultimate in complexity comes in highly functional biological materials with their hierarchical structures, in which there may be no length scale on which the material is homogeneous for any practical purpose. And even if the material is statistically homogeneous, the presence of defects can dramatically alter the properties of the material and is of critical importance in most cases.

The conditions of processing may also be complex. In contrast to (seemingly) simple techniques such as casting, modern materials processing often involves conditions far from equilibrium, including the presence of strong fields (such as electrospinning of polymer fibers) or gradients (such as rapid heating and cooling in laser surface treatments). These conditions may extend beyond processing as well; for instance, a material in a nuclear reactor can be subjected to continuing radiation damage throughout its service life. Whether fundamental to the manufacturing process or evolving through the service life of

the material, the complex evolution history of materials must be understood as the community moves towards predictive process-aware models of material behavior.

Finally, it is important to recognize that all complexity issues are of practical importance in terms of their ultimate effects on the properties and behavior of materials—which are themselves complex, due to the complicated interplay between complex structures, defects, and the environment of the material in service. Historically, the majority of studies of complex materials behavior have been simplified by techniques that probe—or at least are performed under—equilibrium or near-equilibrium conditions. While such simplifications have enabled significant advances, many of our outstanding questions, many of the opportunities to make significant advances, and many of the requirements to reduce uncertainties lie in the area of fundamentally non-equilibrium materials properties and behaviors.

In this report, we describe several key areas for developing a new understanding of the complexity of materials structure, processing, and behavior. In particular, our focus is on areas that could benefit from advances in structural characterization and that would be enabled by new hard x-ray sources, improvements on existing capabilities leading to new understanding, and the ways that x-ray techniques can help forge direct links between computational models and experimental results.

## 5.2  Addressing Complexity with Characterization Utilizing Hard X-Ray Sources

Complexity issues that are related directly or indirectly to the structures of materials can be addressed by structural or microstructural characterization. It is clear that complexity cannot be adequately addressed with techniques that provide only average or mean-field descriptions of structure. For example, the Hall-Petch equation [1] provides a simple relationship between the strength of a polycrystalline metal and its average grain size. While useful and easy to apply, many important aspects of mechanical behavior (such as ductility, toughness, and fatigue resistance) are not amenable to such a simple description. We can build detailed models of materials behavior (for instance by discrete dislocation dynamics simulations), but these models require appropriate input and validation—a task calling for detailed microstructural characterization. What are needed are characterization techniques with the spatial resolution and sensitivity to provide a detailed non-destructive depiction of the structure on appropriate length scales.

A similar comment can be made with regard to temporal resolution. All mechanisms of interest in materials, whether related to materials processing or behavior in service, have fundamental time scales over which they occur. The relevant time scales may range from femtoseconds to years, depending on the process, and both ends of this range present challenge. At the shortest time scales, it is obviously a challenge to implement suitably fast characterization techniques. At the longest time scales, there are issues associated with continuity of the experiment and access to appropriate characterization tools. Even at intermediate times scales there are challenges; it may be possible to make simple before-and-after comparisons of the structure, but these will be misleading if there are transient intermediate steps, in which case *in situ* characterization becomes critical to understanding.

Some of the issues outlined above can be addressed by means of structural characterization using hard (> 5 keV) x-rays. Hard x-rays are convenient because they are more penetrating than electrons, allowing

characterization of bulk materials, but they scatter more strongly than neutrons, allowing characterization of relatively small volumes of materials. Their penetration power, when coupled with small scattering angles, also enables complex *in situ* environments. X-rays also have a variety of useful interactions with materials, including elastic and inelastic scattering, refraction, absorption, fluorescence, and photoelectron emission. Furthermore, x-ray sources of tremendous utility have been developed over the past 40 years. Of particular note in this regard are the high brilliance, coherence, and pulsed time structure of modern third-generation synchrotron sources, and the recent development of even more capable fourth-generation sources such as x-ray free-electron lasers.

In many cases, the level of temporal and spatial resolution for probing these non-equilibrium phenomena is beyond our current or even projected capabilities. Such phenomena may be addressed via suitable modeling. Then the issue becomes how to provide appropriate input to the models, and how to validate their output by comparison to experimental observables. A major challenge and opportunity lies in the paradox that many advances in modeling and simulation are dependent on increasing fidelity in temporal and spatial resolution to the extreme of molecular dynamics (MD), which can track the movement of individual atoms, while many experimental techniques yield data that is averaged over some length and time scale. While techniques such as reverse Monte Carlo (RMC) seek to bridge this gap, opportunities persist to advance the linkage between experimental data and modeling and simulation as both areas advance in their own right (**see Box 1**).

## 5.3  Advances in Structural Characterization Utilizing New Hard X- Ray Sources

The materials science community is in something of a golden age with respect to sources of hard x-rays. Besides the construction of new third-generation synchrotron sources (and upgrades to existing sources such as the APS and ESRF), new types of sources based on linear accelerators are being developed. X-ray free-electron laser sources, such as LCLS at SLAC National Laboratory, provide extremely short bursts of high-intensity coherent x-rays at repetition rates of ~100 Hz. In contrast, proposed energy recovery linac (ERL) source at Cornell University has the potential to provide similar time-average hard x-ray fluxes but at much higher repetition rates of ~$10^9$ Hz. Therefore, XFEL sources will be best for probing events on ultrashort (femtosecond) time scales, while ERL sources will be preferable for continuous, non-destructive studies

In order to realize continued progress in the development of advanced materials and advanced materials processing, an increasingly fundamental understanding of materials will be required. Achieving such an understanding will entail techniques for detailed structural and microstructural investigations on spatial and temporal scales commensurate with the complexity of materials under highly non-equilibrium processing. Considering the inherent capacity of x-rays to interrogate materials nondestructively in 3D on wide ranging length scales, emphasis on the development of high-brilliance pulsed-x-ray measurements under extreme conditions commensurate with the time scales of transient heterogeneities during materials processing will be important.

## Box 1: Probing materials processing from spatiotemporal structural measurements across multiple length and time scales

*"Understanding of the relationships between processing, structure and properties will give rise to the integrated performance of the material in the range of applications and environments that the twenty-first century will require and which the new environments man accesses will impose. This interrelation of structure to processing and its connection to the response achieved in use must be understood to exploit materials for the extreme but also to design new processing routes for the modern world. These paradigms offer an exciting forefront for the future advance of materials and structures constructed from them through the next century."*

In Situ techniques to probe structure and properties at sufficient temporal and spatial resolution to quantify controlling mechanism

Performance Meets Requirements or Modify

**5. Materials/Process Specification**

**1. Design Performance Requirements**

Materials Synthesis Models

Continuum models

**4. Processing**
Primary
Secondary
Fabrication

**2. Material Properties**
Mechanical
Physical
Chemical

Process/Structure Models

**3. Structure/ Composition**
Architecture
Microstructure
Nanostructure

Structure/Property or Green's Function Models

Microstructure image courtesy of E. Lauritsen

*See Reference [10]*

*For Details: Decadal Challenges for Predicting and Controlling Materials Performance in Extremes, Chair, John Sarrao, Los Alamos National Laboratory, April 2010, pp. 91-105*

Pulsed x-ray sources with pulse-widths from hundreds of picoseconds to under hundred femtoseconds exist in the form of synchrotron storage rings, high power pulsed-lasers (XFELs), and inverse Compton scattering of short x-ray pulses. These sources have provided experimental access to fast transient structural properties of materials including deformation during shock loading, rapid laser heating and melting, and photo-induced atomic and crystallographic changes. However, the single pulse photon flux for conventional sources lack the single-pulse full-measurement capability of the sub-100 femtosecond pulses of the LCLS free-electron laser, which contain up to $10^{12}$ hard x-ray photons. The ability to make full diffraction measurements with a single pulse is particularly critical for materials processing investigations such as mechanical stress-induced formation/deformation, pulsed deposition film growth, etc., that are not reversible and, hence, are not amenable to multi-shot measurements to accumulate measurement statistics. On the other hand, single, high-flux x-ray pulse measurements of, say, shock-induced deformation, energetic ion-induced cascade dynamics, or pulsed-laser deposition film growth do not provide access to the overall time evolution of the processes, which can span from one to several orders of magnitude (or more) in time as shock-waves traverse a sample or cascade-induced defects recombine and/or aggregate temporally.

In general, x-ray scattering techniques involving high-resolution area detectors subtending solid angles as large as possible are needed to facilitate comprehensive analyses from single measurements. The development of advanced detectors is being addressed to some extent by the increasingly higher resolution, lower noise, and faster readout area detectors. More difficult, but of potential future importance, will be the development of micro-pulsed high-brilliance x-ray sources capable of approximately 10s to 100s of micro-pulses at a high repetition rate with sufficient flux in each micro-pulse to record full diffraction patterns. Micro-pulsed sources do not exist at present; neither do such high-speed area detectors, at least in the picosecond or nanosecond regime. However, pixel array detectors operating in the sub-microsecond regime are available.

## 5.4  Coherency

The development of third- and fourth-generation hard x-ray sources with high transverse coherence creates new opportunities for structural characterization of materials. For instance, coherent diffraction imaging can be used to examine the structure of nanoparticles in three dimensions [3]. It is even possible to map strain fields inside crystals in three dimensions [4], a capability with tremendous potential for advancing our understanding of deformation processing of materials.

An even more exciting possibility enabled by coherency is the use of x-ray speckle to study the dynamics of self-organization and defects in materials. This technique is called x-ray intensity fluctuation spectroscopy (XIFS), or x-ray photon correlation spectroscopy (XPCS) [5]. In a disordered material, speckle in a diffraction pattern results from constructive interference among random x-ray scatterers within a material. As the scatterers move, the speckle intensity fluctuates and the underlying dynamics can be determined. In a small-angle x-ray scattering (SAXS) regime, this approach shows great promise for advancing our understanding of the behavior of colloids, polymers, and other soft materials. Another area of interest is using the fluctuations in speckle in coherent Bragg diffraction to observe dynamics of defects and phase transitions in metals.

## 5.5 Opportunities for Advances Utilizing Existing Sources

Developing new, advanced x-ray sources obviously will require significant resources and take years if not decades to bring to fruition. In the meantime, we already have tremendously powerful tools at our disposal in the form of third-generation synchrotron sources and XFELs. The availability of the third-generation synchrotron sources has already led to tremendous advances in our understanding of materials and materials processing, but it is also clear that there is room for improvement in the use of third-generation sources and in utilizing XFELs in the future. In some cases these improvements will require new technological advances, but in other areas relatively simple changes to facilities and operations would be beneficial.

### 5.5.1 Detectors

One area of emphasis needs to be continued development of advanced x-ray detectors with improved temporal, spatial, and energy resolution. Many current experiments are constrained more by limitations of detectors than by the characteristics of the source. For example, self-propagating exothermic reactions in metallic multilayers involve structural evolution over time scales of ~100 μs. Existing sources have plenty of flux to investigate these transformations at the microsecond level, but few detectors are capable of capturing data continuously at frame rates of ~1 MHz, and those that are suffer from limitations in spatial resolution or format (physical size). Similarly, fast area detectors with good energy resolution would be a boon, enabling, for example, resonant x-ray scattering studies to obtain species-specific structural information. Combining detectors into arrays for simultaneous measurements on different length scales will become increasingly important, with examples including wide- and small-angle scattering as well as semi-transparent detectors for near- and far-field x-ray imaging utilizing high-energy diffraction microscopy.

### 5.5.2 Addressing Complexity with Informatics

The use of hard x-rays provides unique opportunities to conduct in-situ experiments and thereby explore both length and time scales associated with the dynamics of materials processing. The multidimensionality associated with the large number of materials and process variables creates a level of complexity that needs to be unraveled if one is to fully exploit links between atomistic scale behavior and macroscopic characteristics of materials processing. This in turn requires the development and utilization of data science based computational tools, i.e. informatics tools that handle, analyze and help interpret complexities in data acquired through such experiments. Statistical learning methods can be applied to both simulation based data as well as experimental scattering data to predict a priori the outcome of materials processing steps outside known heuristic information. In a complementary manner, informatics as applied to materials discovery and design can identify new structure-bonding correlations that need to be studied utilizing hard x-rays. Hence informatics can be applied to both ends of the information spectrum before and after the experiment.

A related issue is how large and/or complex data sets can be handled effectively by researchers utilizing advanced x-ray sources. Even routine experiments can collect hundreds or thousands of diffraction patterns or images over the course of several days of beam time at a modern source. Individual

researchers can work through their data after a run is complete, but the ability to do preliminary data analysis on the fly at the beam line would greatly improve the efficiency of these experiments by allowing mid-run course corrections to the experiment. Greater levels of collaboration and efficient use of data through informatics methods will be made possible through investments in structured storage of and access to raw and processed data together with metadata.

Much of the interpretation of x-ray experiments is built around utilizing some form of correlation analysis, such as correlative x-ray microscopy/scattering angular intensity which can deliver information on local bond arrangements in a disordered (or partially ordered) system. Statistical learning methods are effectively *n* point correlation methods that can accurately and rapidly survey across time and length scales without the restrictions of assuming the exact physics and in fact can potentially discover new physics. Many examples of the types of studies discussed by this panel could be significantly enhanced with informatics, if not provide a transformative role in the field of hard x-rays (**see Box 2**). Following topics will be of great importance in future studies:

- *Use of data mining methods to link high-resolution time-resolved x-ray measurement and simulations techniques for the study of the dynamical behavior of materials out ofequilibrium*

- *Statistical learning to explore the linkages between high temporal and spatial resolution probes of materials structure, microstructure, evolution and dynamics.*

- *Manifold learning to unravel the complexity the thermodynamic and kinetic phase space involving transformations between vapor and bulk condensed for fundamental studies of nonlinear dynamics to get insight into the nature of the chemical mechanisms involved in synthesis of metastable materials*

- *Use of data clustering methods to develop calibration models involving improvements in x-ray flux and detector cycling speeds, or the incorporation of pump-probe methods that will enable us to move into the microsecond time domain, and beyond, to study the early stages of solid growth from supercooled liquids*

- *Use of association mining tools to develop voxel by voxel correlations between microstructural features utilizing different modalities of imaging such as high-energy diffraction microscopy (HEDM), in which grain and sub-grain volumes are mapped in polycrystalline aggregates, combined with small- and wide-angle x-ray scattering (WAXS), which permits information over a broad range of length scales to be collected from the same (micron-level) volume Application of data mining methods linked to high-performance computing to track linkages in real time between ultra-short time scale materials dynamics (e.g., shock loading) with ultra-high spatial resolution.*

### 5.5.3 In Situ Experiments and Combinations of Techniques

In many cases, it is clear that adequately addressing the complexity of materials and materials processing requires the application of multiple complementary characterization techniques. At its simplest, application of classic characterization techniques, along with more advanced techniques enables direct comparison of the new results and discoveries with an often expansive library of data. There is more power in employing multiple probes to diagnose an experiment that will enable

correlation measurements of numerous phenomena across multiple temporal and spatial scales. Simultaneous use of *in situ* techniques is particularly important when studying processes that are non-repeatable and stochastic.

For example, calorimetry is a useful adjunct to x-ray scattering for examining nucleation and growth of crystalline phases in glassy precursors. Similarly, structural characterization of surfaces by x-ray techniques becomes more powerful when combined with surface chemical characterization (e.g., Auger electron spectroscopy). Use of combined x-ray techniques including small- and wide-angle scattering or scattering plus imaging, allows simultaneous access to length scales relevant for studying complex processes ranging from nanoparticle evolution [6] to biological tissue hierarchies [7]. A key advantage of hard x-rays for studying materials processing is their penetration power, which enables structural studies of materials in realistic environments. Myriad non-equilibrium conditions are desired in modern day experiments, including rapid cooling in amorphous and nanocrystal processing, ultrasonic- and laser beam-induced reactions in vapor syntheses, and microwave catalyzed reactions. The processes involved in such technologies include oxygen smelting, welding, spray forming, metal atomization by electric fluid dynamics, and structural modification (by shot peening, for instance). In addition, there is a trend for simultaneous multi-dimensional system perturbations such as temperature, pressure, and irradiation. Another novel environment under development is containerless processing, which can be used to reveal liquid structure in the deeply supercooled state, and corresponding phenomena of homogeneous and heterogeneous nucleation; such experiments are described below.

To fully exploit the potential of x-rays, therefore, it is essential that we continue to develop new capabilities for examination of materials in a variety of conditions, and to make these capabilities available to as wide a range of potential users as possible.

# Box 2: Next-Gen Microelectronics, Solar-Cells, and Blue Gene

*Determining and controlling the location and size of dopant or impurity atoms and their clusters, and characterizing their valence and electronic structure is the biggest challenge in materials processing for the next-generation Si microelectronics and low-cost Si (SoG-Si) solar cells.*

*Aptly, this has been referred to as <u>discovering the "inorganic gene" in complex inorganic solids</u> . Optimized inorganic gene engineering of metal atoms, clusters, and defects could lead to new cost-efficient silicon technologies. To achieve this we need newer x-ray imaging methodologies to unravel the evolution of complexity of structural and correlation maps of dopants, impurities, and defects.  Modeling these maps requires a host of tools: Blue Gene supercomputers that can parallel process extremely large data sets, and data mining algorithms that can be used to make robust clustering and correlation analyses, which is critical in discriminating between atomic chemistries ( See: Sudip Seal, Michael Moody, Anna Ceguerra, Simon Ringer, Krishna Rajan, Srinivas Aluru, Tracking Nanostructural Evolution in Alloys: Large-scale Analysis of Atom Probe Tomography Data on Blue Gene/L, ICPP '08. 37th International Conference on Parallel Processing, 338 – 345, 2008).*

*In the following case study, metal nanodefect engineering is used to reduce the electrical activity of metallic impurities, resulting in dramatic enhancements of performance even in heavily contaminated solar-cell material. Highly sensitive synchrotron-based x-ray fluorescence measurements (see figure) can describe the spatial and size distributions of metal nanodefects that regulate the minority-carrier diffusion length, a key parameter for determining the actual performance of solar-cell devices. (Tonio Buonassisi, Andrei A. Istratov, Matthew A. Marcus, Barry Lai,  Zhonghou Cai, Steven M. Heald, Eicke R. Weber, Engineering metal-impurity nanodefects for low-cost solar cells, Nature Materials, 4, 676-679, 2005).*



FeSi$_2$ nanoprecipitat

Micrometer size Fe$_2$O$_3$ inclusions
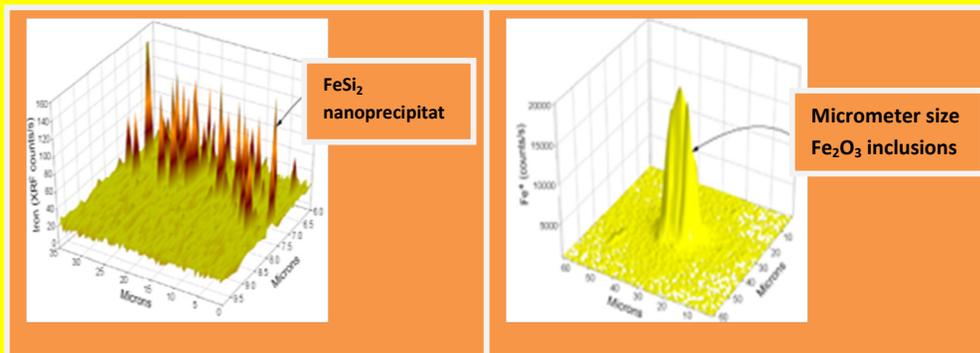
Metallic glasses offer a complex system in which the power of combining advanced x-ray techniques with selected non-x-ray techniques can be demonstrated. In such cases it can be illuminating to investigate with care the mechanisms of formation and of recrystalliztion. To determine the short- and medium-range order, one can apply the pair distribution function (PDF) technique, utilizing high-energy x-rays to measure out to large values of momentum transfer, $q$. This enables accurate Fourier transformation of the data, and thus a robust analysis. Equally important is how the glass or amorphous material transforms out of the disordered phase. Chen and Spaepen suggest isothermal calorimetric measurements for differentiating between liquid-like structure and nano- or micro-crystalline structure in a glass [8]. They argue that isothermal calorimetry of a microcrystalline structure will show a monotonically decreasing thermal signal of transformation characteristic of simple grain growth to a coarser polycrystalline assembly, whereas isothermal calorimetry of an amorphous glass structure will show a peaked signal indicating transformation by nucleation and growth. Combined isothermal calorimetry and high-resolution x-ray diffraction and micro-PDF capabilities would allow for the investigation and characterization of disordered materials, leading ultimately to understanding the fundamentals of tailoring materials properties to technological needs.

## 5.6  Example: Pulsed-Laser Processing and Pulsed-Deposition Film Growth

High-powered laser pulses with the ability to ablate material from surfaces provide the basis for pulsed-laser deposition (PLD) film growth. The ability of PLD to transport target source material to substrates congruently has made PLD an important technique for the synthesis of thin films and multilayers, especially complex materials such as high-temperature superconductors, manganites, and multi-ferroic materials. However, because of the highly non-equilibrium nature of the ablation process and the presence of a plasma plume at the substrate surface as the energetic and non-equilibrium pulse of material is deposited, many aspects PLD film growth are not fundamentally well understood. As a result, the selection of parameters such as the laser wavelength, power density, pulse length, pulse repetition rate, target to substrate distance, substrate temperature, and buffer or oxygen (for oxides) ambient gas pressures is based largely on empirical knowledge and prior experience recipes.

 While the remarkable success of PLD epitaxial growth for complex materials without a full understanding of the underlying science of the mechanisms is a testimony to the robustness of the technique, it is also a signal that only a fraction of the capabilities of PLD for the production of synthetically engineered materials with new structures and novel properties are being exploited in terms of complexity, perfection, and speed. Areas in which key information is missing are the ablation process itself (including the time, temperature, and spatial profiles of the processing of the source target) and the dynamics of the deposition and crystallization process (including the kinetic energy, the ionization state, the temperature, and the cluster vs atomic species nature of the target material as it is deposited) on the substrate.

Figure 5.1 illustrates schematically (1) a femtosecond-to-nanosecond laser pulse striking the target, (2) the transport of an ablated pulse of material from the target to the substrate, (3) the interaction of the plume with the substrate and deposition of the ablated material on the substrate surface, and

(4) the formation of an epitaxial thin-film layer following thermal surface transport for time scales typically varying from milliseconds to seconds given by the dwell time between ablation pulses.

Sophisticated spectroscopy measurements and modeling have been performed on the plume propagation and composition through the ambient atmosphere of ablation chambers and on the structure and morphology of the epitaxially-grown films and multilayers during the dwell time between laser pulses. However, critical time- and depth-resolved structural and temperature measurements are needed in connection with detailed first principles simulation and modeling of the interaction of the laser ablation pulses with the target surface and subsurface to understand the complex and highly non-equilibrium nature of the solid, liquid, and plasma aspects of the ablation process itself; and to determine the range of material compositions and structures, velocities, temperatures, etc. that can be achieved for the ablated species as a function of laser pulse power densities, pulse length, pulse shape, dwell times, etc. for insulating, semiconducting, or metallic materials. The fundamental difference between the near-equilibrium characteristics of molecular beam epitaxial growth and the inherently non-equilibrium characteristics of PLD is profound in terms of the range of phase space that is available for synthetically generating new materials. A fundamental understanding of ablation characteristics for pulse lengths ranging over the six orders of magnitude from femtosecond to nanosecond is needed to control and exploit pulsed growth opportunities.

This will entail picosecond-to-femtosecond range temporal resolution x-ray diffraction and optical spectroscopy probes along with detailed depth- and time-resolved structural and spectroscopic simulations and modeling as benchmarks of understanding.

Clearly, both the temporal resolution and the high photon flux per pulse associated with free-electron laser x-ray sources are needed, even for measurements into the nanosecond and μs regimes because of the requirement of single-shot x-ray diffraction measurements of structure, thermal expansion induced dilatations, solid-liquid transformations, void generated porosities, and depth dependent gradients of these properties. Techniques for extracting these properties quantitatively are not straightforward even with the availability of intense FEL x-ray pulses; however, in principle, diffraction signatures exist for all structural changes.

A fundamental understanding of the pulsed laser ablation process in connection with how the ablated material interacts as it propagates through
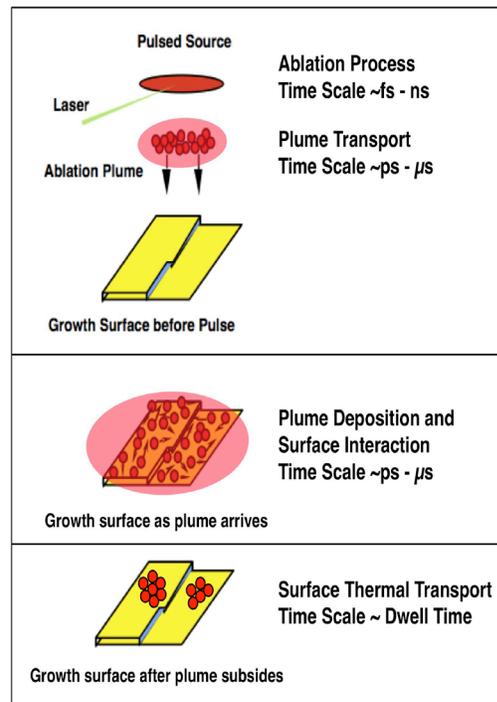


*Figure 5.1  Pulsed-laser deposition process: (upper) femtosecond-nanosecond laser pulse ablates target material into a plume that is transported to the substrate on microsecond time scale; (middle) plume of ablated material arrives at substrate; (bottom) growth surface following dwell time between laser pulses*

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the chamber ambient gas atmosphere would provide the ability to control the nature of the (electronically and kinetically) excited ablation plume as it impinges on the substrate. However, an understanding and control of the kinetics and dynamics associated with the epitaxial crystallization of material as it lands on the substrate and evolves within the plasma plume is presently not available. Time-resolved x-ray surface diffraction measurements have shown that epitaxial crystallization occurs on time scales faster than a few tens of microseconds under nanosecond regime laser ablation pulses (yielding a few microseconds deposition time); however, it is likely that the crystallization process occurs on time scales faster (and possibly much faster) than the deposition rate.

As a result, it is presently not known what limitations exist on the rate of growth and the range and complexity of structures that can be synthesized under the highly non-equilibrium conditions achievable with PLD growth by appropriately varying the ablation and chamber ambient conditions. Because of the weak scattering rates for surface truncation rod x-ray diffraction during epitaxial film growth, third-generation synchrotron sources are not capable of single shot nanosecond or microsecond measurements even though ~50-100-ps x-ray pulses are available at third-generation synchrotrons. Moreover, investigation of the fundamental aspects and ultimate rate limitations on epitaxial crystallization and evolution will entail measurements under femtosecond and picosecond ablation conditions with laser deposition plume conditions ranging from, say, picosecond to nanosecond in addition to the μs deposition rates associated with nanosecond ablation conditions and relatively high oxygen and buffer gasses typically used for oxide PLD growth. Therefore, ultra-high-brilliance x-ray pulses in the picosecond or sub-picosecond width ranges will be required. Moreover, consideration should be given to the potential for generating a series of micropulses with variable spacing in addition to the present single, ~100-Hz x-ray pulses. Of course this would entail techniques for the detection of individual micropulses; however, the ability to measure the full evolution of crystallization for a single ablation pulse, as opposed to making measurements for only a single time point in the evolution of individual PLD growth pulses, would be transformational.

Increasingly, x-ray methods are being developed to characterize individual grains and local defects without the need for grain-averaging. Utilizing either monochromatic or polychromatic beams, these methods provide structural information analogous to electron backscattering — including grain boundary topology, strain state and orientation— ut non-destructively, allowing *in situ* studies under realistic material-constraint conditions. Currently, several thousands of grains can be mapped for adequate statistical analysis of heterogeneity, while individual grain nucleation and growth can be followed *in situ*. These methods can be combined with high-resolution reciprocal space mapping, which is sensitive down to the nanometer length scale, to probe evolving dislocation structures. Such experimental data are crucial for development of physical models such as sub-grain finite element calculations. Developments related to third- and fourth-generation sources will push spatial resolution limits to sub-micron levels, and can provide high-fidelity starting point structural data crucial for the molecular dynamics simulations discussed in this document.

## 5.7  Example: High-Rate Deformation

A comprehensive understanding of microstructure-based heterogeneity and its consequences for materials damage and failure, and phase transformation initiation during high-rate deformation (shock loading), is presently lacking. Concentration and spatial variability in compositional and dissipative defects add to the difficulty of understanding dynamic effects in polycrystalline microstructures. Dislocations can be activated /nucleated and phase boundaries can be crossed during dynamic deformation. Many materials also produce twin- or slip-band structures with deformation that produce further heterogeneity within individual crystals. Future tools will be needed to probe the physics of dynamic solid-solid phase transformation and damage at length scales approaching those at which they nucleate in order to gain a detailed understanding of this process and the influence real material microstructure has on these events. The extreme conditions encountered under dynamic loading provide the setting to explore the interplay between mechanical and thermal processes in these complex systems.

Experiments of interest would include the determination of melt curves, crystal structures, phase stability and metastabilty, microstructures and mechanical strength, and chemical bonding over a broad range of pressure, temperature, and time. Model experiments might include low-Z to high-Z materials in single and polycrystalline forms, and span orders of magnitude in length and time scales.

The investigation of material processes leading to ductile spall in polycrystalline metals would help to bridge the gap between *ex situ* observations and physical processes included in molecular dynamics and mesoscale models. As a starting point, such models also require accurate determination of kinetic and thermodynamic contributions to phase behavior in dynamically loaded single crystals. The evaluation of the relative importance of defect evolution and phase transitions in single-crystal explosives would provide direct information to molecular dynamics simulations, which have identified both features in static and dynamic loading simulations, but to this point lack experimental confirmation beyond mere coincidence. In the long-standing issue of explosive initiation, investigation of the microstructural contributions that ultimately lead to increased susceptibility to reaction initiation and detonation might resolve questions that have lingered for many decades and would prove fundamental to safety models for these materials. There are also cases where explosive materials exhibit reaction pathways that are of importance in understanding their performance function; a linked dynamic spectroscopic and structural probe would be useful in resolving chemical reaction dynamics at detonation speeds (many km/s). These systems described are prime targets for investigation with next-generation hard x-ray tools, and each represent opportunities for significant experimentation and leaps in theoretical understanding and bridging gaps in length/time scales. Experiment design for all will be a balance of time and resolution needs, ensuring accurate loading states, and designing photon number, coherence, and energy for desired penetration and focusing while avoiding or accounting for beam degradation in the sample.

As a complement, it is important to include traditional diagnostics on experiments. This is not simply because we are accustomed to fielding them on such experiments, but because linking the advanced tools to the traditional diagnostics unlocks much historical data for more enlightened interpretation. Also, getting as much information as possible from a single experiment can help resolve questions about

experimental variation. The initial limitation in high-rate loading experiments will be detector technology. Advances in time-resolved diagnostics will be needed to take full advantage of even existing light sources. However, as detection technologies progress to the needed time resolution, photon numbers will limit possible resolutions, and ultimately this will require more advanced sources.

## 5.8 Connections to Large-Scale Atomistic Simulations

A key to maximizing the impact of experiments aimed at probing the complex behavior of materials is the availability of theoretical and numerical frameworks to highlight and interpret the fundamental underpinnings of the phenomena. In this respect, very few methods share the predictive power of fully-atomistic molecular dynamics simulations. Indeed, because MD proceeds from a fundamental standpoint—it consists of the integration of the atomic equation of motion—simulations are free from near-equilibrium assumptions and have the potential to reveal the whole range of complex emergent behavior characteristic of a large number of interacting entities. However, this predictive power comes at a rather high computational cost: even on a petascale computer, simulating a micron-sized chunk of material for a few tens of nanoseconds is a heroic feat. Decreasing the number of atoms to tens of thousands only allows for an extension of the time scales up to a microsecond at best because of code-scalability issues. Given these constraints, a self-contained reproduction of the experiments with MD is limited to ultra-fast processessuch as ductile spall following shock loading or the relaxation of collision cascades following irradiation, for example. In these cases, simulations have demonstrated their ability to capture the mechanisms of defect formation, growth, and interaction, and to reveal the characteristic features of these processes at larger scales.

Realizing that many phenomena of practical and fundamental interest occur on timescales that greatly exceed nanoseconds, methodological improvements aiming at extending the reach of MD without compromising its predictive power have been developed over the last decade or so. Notable in that respect are the accelerated molecular dynamics (AMD) methods [9], where known properties of systems evolving through a sequence of rare, activated events are exploited in order to generate statistically correct long-time trajectories at an affordable computational cost. These methods open up a time-window—ranging from microsecond to seconds—that is often crucial to achieve correspondence with experiments. One of the drawbacks of such an approach, however, is the limited size that can be simulated, usually ranging from 1000 to about 100,000 atoms. These techniques are therefore more powerful when a clear atomistic target, i.e., a specific microstructural feature, is identified as a precursor to the complex phenomena of interest. If this can be done, AMD techniques have demonstrated—for example in the case of slow mechanical deformation of nanostructured materials or of slow, diffusion-driven, microstructural evolution—their ability to accurately bridge the timescale gap that separates simulations from experiments. These techniques are also ideal to inform larger-scale models, like kinetic Monte Carlo or mesoscale plasticity models, which can provide a more direct connection with experimental measurements.

In all of the aforementioned cases, however, reliable support from atomistic simulations is conditional on a very good, ideally atomic-scale characterization of the initial conditions. If this admittedly strict

condition can be achieved, the interplay between simulations and future x-ray experiments will without a doubt shed a new light on the origin and characteristics of the complexity emerging from materials pushed out of equilibrium.

The need for such high-fidelity experimental data, taken under non-equilibrium conditions, has led to *Matter-Radiation Interactions in Extremes (MaRIE)* initiative [10] at Los-Alamos National Laboratory. MaRIE is comprised of three pillars, namely a Fission and Fusion Materials Facility, Multi-Probe Diagnostic Hall, and M4 (Making, Measuring, and Modeling Materials) Facility for materials synthesis, characterization, and integration. These requested facilities would include a fourth-generation light source (x-ray FEL) with an intense irradiation environment of a proton-beam spallation neutron source, to provide *in situ* measurements of material conditions in a radiation environment and measure radiation damage phenomena with unprecedented temporal and spatial resolution. Such a facility would complement existing hard-x-ray sources and be of relevance to many of the scientific examples provided in this document.

## *5.9 Dynamics and Evolution of Atomic Displacement Cascades*

When materials are exposed to energetic ion implantation processing or radiation environments of fission or fusion neutrons (energies of ~2-10 MeV), direct collisions of ions or fast neutrons with lattice atoms result in a cascade of atomic displacements and the deposition of several tens of keV of kinetic energy in a volume with a few nanometers diameter [11]. This is the fundamental origin of radiation damage in materials, and the environment within cascade regions constitutes one of the most extreme conditions for materials. Moreover, the highly excited, high-temperature, defect-rich conditions prevailing within atomic displacement cascade regions are some of the most transient. According to molecular dynamics simulations of cascades, the process involves the displacement of thousands of atoms within nanoscale volumes on sub-picosecond time scales [12]. As discussed below and demonstrated in Fig. 5.2, MD simulations predict a sub-picosecond defect generation phase followed by a rapid quenching phase in which the vast majority of the vacancies and interstitials annihilate one another in recombination reactions, and within a few picoseconds, disperse the deposited energy by high local thermal gradients.

The temporal evolution of the vacancy-interstitial pairs in cascades predicted by MD as a function of the so-called primary knock-on atom (PKA) energy [13] is shown for iron in Fig. 5.2. Figure 5.3 shows MD spatial configurations at the time of peak damage (~500-900 fs) and after annealing and agglomeration into clusters at ~20 ps.

Although cascades have been the subject of vigorous investigation by MD since the 1960s [14], real-time structural measurements of cascade dynamics to confirm the actual time scales, the temperature distributions, melting vs. non-melting character, the point defect distributions, or the point defect aggregation processes have not been possible on the picosecond time scales needed. Post irradiation measurements have been performed on cascade damage induced by ions and fast neutrons [11, 15] and x-ray and neutron diffuse scattering cascade measurements have been made on materials irradiated at low temperature in order to freeze the cascade damage structure, but the structural dynamics associated with the formation and initial recombination in cascades are not available in such studies.



*Figure 5.2  Time scale of displacement cascade generation of vacancy-interstitial pairs in iron at 100 K for different PKA energies [13].*
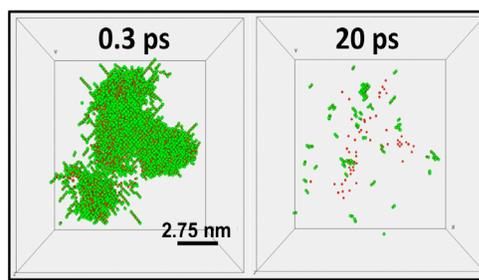


*Figure 5.3  Spatial distribution of defects for a 20 keV pka cascade in iron: (left) defects at 300 fs, and (right) spatial distribution showing clusters and point defects at 20 ps [13].*

The sub-100-fs temporal resolution and the high photon flux ($10^{12}$ photons per pulse) obtainable with the LCLS x-ray free electron laser source now make it feasible to consider single-shot x-ray diffraction measurements of the local structural dynamics of cascades. The pump-probe geometry for such time-resolved measurements is shown schematically in Fig. 5.4. Although extracting cascade dynamics properties quantitatively is not straightforward even with the availability of intense hard x-ray FEL pulses, if sufficiently large photon fluxes are available within a single sub-picosecond pulse to separate background scattering from samples from the cascade signal, analysis techniques described by Larson [16] can be used in connection with insight from cascade simulations [11, 17, 18]. Both forward diffraction (small-angle scattering, coherent imaging, etc.) and Bragg diffuse scattering can be expected to provide information on the local lattice disturbances induced by cascades. By varying the time delay between the arrival of the ion (or ions) and the arrival of the probing x-ray pulse it is possible to construct a statistically based understanding of cascade dynamics recognizing that the detailed structure of each cascade is unique **(see Box 3).**
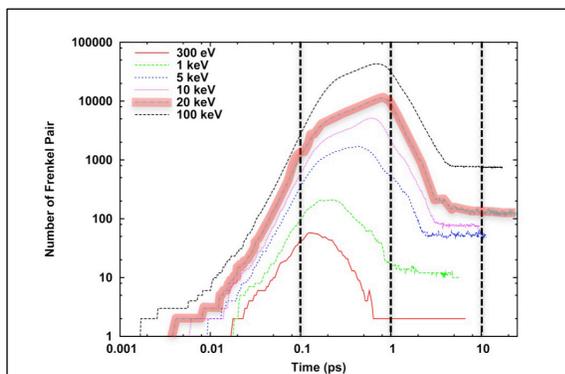
*Figure 5.4  Schematic of a pump-probe time-resolved investigation of cascades generated by energetic ions, where the arrival of an ion (or ions) from a pulsed ion gun is synchronized with the*

Just as with pulsed laser ablation (mentioned above), ion cascade investigations would benefit from a series of closely spaced micropulses such as will be available from the Euro-XFEL in Hamburg, in addition to the ~100-Hz x-ray pulses available at the LCLS, considering that cascade evolution on time scales from picoseconds to milliseconds are of interest. Techniques for charge-coupled device detection of individual micropulses would have to be developed for such micropulses, but the ability to probe the longer time evolution of defect aggregation and accumulation on time scales shorter than the ~10-msec repetition rate would make it possible to compare measurements with simulations.

## 5.10  Solid/Liquid Phase Evolution Utilizing Containerless Processing

Containerless processing offers a unique opportunity to study the structure of liquids in the deeply super-cooled state, and the corresponding phenomena of homogeneous and heterogeneous nucleation. David Turnbull observed that the temperature of many liquid metals could be decreased below their equilibrium melting temperatures before crystallization occurred. Because the densities of metallic liquids and crystals are so similar, it had been widely assumed that the short-range order in the two phases must be similar, which would suggest that the barrier to nucleation of crystalline phases ought to be small. Turnbull's observation that the undercooling of liquid metals could be quite large (~15% of the absolute melting temperature) was therefore unexpected. Charles Frank suggested that the structure of liquid was actually quite different from that of the crystalline solid, containing a significant degree of icosahedral short-range order (ISRO). Surprisingly, Frank's hypothesis [19] was only unambiguously confirmed by experiment very recently, by combining electrostatic levitation (ESL) and high-energy synchrotron radiation scattering techniques.

The primary impediment to quantitative experimental investigations of both solids and liquids at high temperature is contamination. Within the past 20 years, containerless solidification methods have become possible, allowing super-cooling studies of samples with diameters ranging from millimeters to centimeter sizes. Such techniques eliminate the largest source of contamination, the container itself, and techniques have been developed for the measurement of physical properties such as the liquid density, surface tension, viscosity, specific heat, magnetization, and most recently, the liquid structure in

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equilibrium and non-equilibrium liquids*. For the first time it is possible to obtain quantitative information on the nucleation barrier in concert with changes in other physical properties and to couple all of these with the evolution of the liquid structure. These techniques are not limited to liquids, however. They also allow contamination-free studies of structure, phase transitions, and thermophysical and magnetic properties of solids at very high temperatures, providing critical information for demanding technological applications.

While containerless studies via a variety of levitation methods have been possible for some time, the electrostatic levitation (ESL) technique allows investigations that were not previously possible. ESL allows studies of a wide range of materials including insulators, semiconductors and conductors. Moreover, it is possible to precisely control the sample position, stability, heating, and thermal gradients, thus allowing for unprecedented experimental control. At the same time, there have been exciting advances in x-ray scattering techniques and technology, including the realization of the current generation of x-ray sources, the promise of future sources, and the development of efficient area detectors for fast data collection [20]. The ability to coordinate investigations of structure with thermophysical, magnetic, and electronic properties at high temperatures (while avoiding problems of environmental contamination) will enable pioneering studies of short- and medium-range order in liquids above and below the liquidus temperature, liquid -liquid phase transitions, phase-transformation kinetics during solidification and their effect on materials processing, evolving order in systems undergoing structural transformations, and the detection and characterization  of metastable phases and their structures. All of these topics bear directly on, and will have a broad impact upon, the fundamental science of the formation and growth of solid phases and their relationship to their parent liquid phases. The absence of a container or gas flow around samples for ESL allows liquids to be more deeply super-cooled, a feature that has already enabled new high-impact investigations of the relationship between the liquid and solid phase structures in simple metals and intermetallic alloys. Metastable phases at high temperature are notoriously difficult to characterize through standard techniques such as rapid quenching. The ability to *determine in  situ* both the structure and properties of these metastable phases, their formation with composition and temperature, and their role in the formation or inhibition of stable phases at lower temperatures will add tremendously to our understanding of stable phase formation in complex systems.

In this manner, x-ray measurements of microscopic structural evolution can be correlated with techniques such as high resolution thermal imaging to clearly characterize the liquid/solid interface in bulk samples.

# Box 3: How do nanocrystalline grains in copper heal after suffering radiation-induced damage?

*The MD work demonstrates how the grain boundaries (GBs) can serve as effective sinks for radiation-induced defects such as interstitials and vacancies. With the use of three atomistic simulation methods, the temperature-accelerated dynamics (TAD) of the defect–grain boundary interaction mechanisms in copper, from picosecond to microsecond time scales, have been predicted. Selected snapshots of damage self-healing near the GB from TAD simulations are show below.*

*Xian-Ming Bai, Arthur F. Voter, Richard G. Hoagland, Michael Nastasi, Blas P. Uberuaga, Efficient Annealing of Radiation Damage Near Grain Boundaries via Interstitial Emission, Science 327, 1631 – 1634 (2010)*
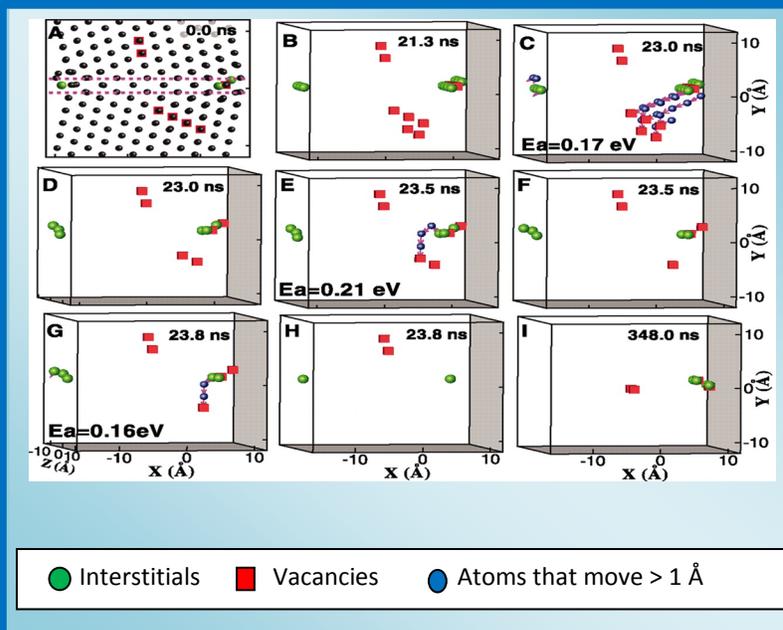
As a second example, extending the range of small angle x-ray scattering, utilizing high energy beams, to $Q$-ranges below 0.001 Å$^{-1}$ will open up new horizons for investigations of phase separation and the development of microstructure on mesoscopic length scales. Although the pace of detector development over the past decade has been breathtaking, further advances allowing for data collection again utilizing high-energy x-rays, over a wide range of $Q$ on sub-microsecond time scales, will allow us to probe the structure of liquids to even deeper undercooling and enable investigations of transient metastable phases upon solidification.

## 5.11 Conclusions

Materials processing is primarily concerned with understanding the development of microstructure, which occurs over a variety of length scales and is inherently complex. There are many opportunities for exploiting the unique capabilities of hard x-rays for studying structural evolution, and these will only expand with the development of new x-ray sources (as well as new capabilities at existing sources). In particular, the ability to probe structural evolution in small volumes on short times scales utilizing the extremely short pulses of XFELs, and the ability to track changes continuously utilizing the proposed ERLs, will provide new insights into fundamental aspects of microstructural change. Equally important will be the use of coherent scattering to understand the dynamics of disordered materials.

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# 6 Focus Panel: Non-equilibrium Chemical Reactions

| | | |
|---|---|---|
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| | *Walker, Richard* | *Diamond Light Source Ltd.* |

## 6.1 Introduction

Non-equilibrium chemical reactions, featured by the directionality and irreversibility of the processes, are present in various natural and manmade systems from cell growth to geological evolution and from catalytic converters to energy storage devices. Compared to equilibrium chemical reactions where the system remains at a steady-state for extended time, the non-equilibrium processes are less well understood due to the complexity connected to the energetics and dynamics as well as structural evolution along the reaction path. A chemical reaction can be viewed as an equilibrium or non-equilibrium process depending on the time window and the spatial scale through which the observation is made. An equilibrium process could become a non-equilibrium process under an external driving force, such as a pulse of light, heat, electric/magnetic field, etc. The non-equilibrium processes lead to chemical transformations, which bring changes that are important in nature as well as in our lives. Scientists have utilized different external forces to drive chemical transformations, but how these external forces act on electrons and atoms is not completely clear. This is a serious obstacle for chemical science to overcome by rationally controlling the reactions at appropriate rates that lead to desired final products.

The availability of hard x-ray sources in recent years has made it possible to measure atomic-level views of non-equilibrium phenomena in inorganic, molecular, and biomolecular systems. As background material for this report, we refer the reader to a set of exhaustive articles in a special issue of *Acta Crystallographica,* Section A: Foundations of Crystallography, Dynamical Structural Science, edited by Eric Collett [1]. The articles demonstrate the diversity of this field that covers the understanding of dynamical evolution of non-equilibrium structures in solid state physics, molecular materials, biological molecules, and molecules in solution. The time scales of interest span from 100-fs atomic motion dynamics to slower (μs) molecular diffusion and microsecond relaxation processes of transient excited states.

This focus panel addressed the following challenges and perspective in driving and understanding non-equilibrium processes at the electron and atom levels, all of which represent non-equilibrium chemical behavior.

The three areas covered by the focus panel included:

a)      Chemical reaction dynamics: structure of the transition state
b)      Quantum control of chemical reactions
c)      Dynamic propagation of the reactions

## 6.2 Chemical Reaction Dynamics: Structure of the Transition State

Almost all chemical reactions result in molecular structural changes in the reactants. Although many initial structures of reactants and final structures are well known, very few direct experimental observations are available about the electronic/atomic pathways along the reaction trajectories with the same accuracy as those obtained in steady-state structures. The complexity comes from the dynamic

nature of molecules along a reaction trajectory where the energy, structure, and time required for the transformation steps vary.
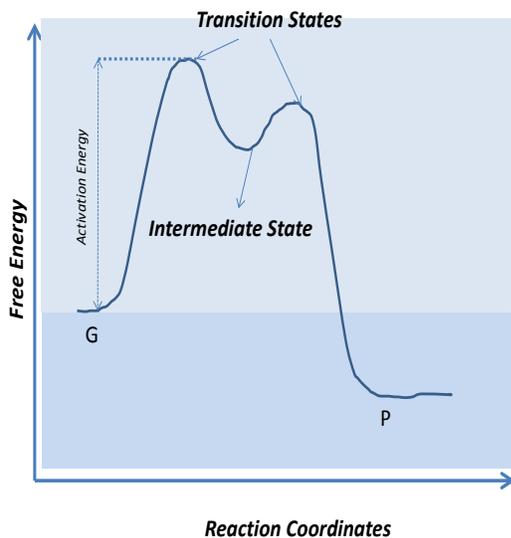


*Figure 6.1  A one-dimensional pathway of a reaction with an intermediate state is in the trough between the two transition states. G represents the ground, and P represents the product.*

A theoretical description of the reaction pathway has led to the concept of the system evolving through the so-called "transition-state region," and this is one of the most important concepts in chemistry (Fig. 6.1). It represents a singularity at the intersection of the energy surfaces at the top of the potential barrier crossing trajectory where the small fluctuations take the system from nuclear configurations defining the reactant to those of the product state. It is believed that a TS has no lifetime or a barrier crossing time, which at best can only be a fraction of the vibrational period. There are fairly detailed microscopic models of such processes in which specific structures are proposed for motion along the reaction coordinates [2]. However, almost all time-resolved structural studies in disordered phases have so far identified transient or intermediate structures that equilibrated in an excited state or in a TS potential-well rather than the associated coherent atomic or electron motions [3]. Hence, the TSs have been elusive from experimental observation especially in the solution phase.

The seminal work of Marcus [4] presents a comprehensive approach to understand the large amount of optical data collected on electron tranfer (ET) reaction rates in organic syntheses. The key parts that determine the rate equation are the Frank-Condon term describing the overlap of vibrational wave function of the reactants and the product, and the so called "overlap" term that describes the overlap of electronic wave functions of the reactants and the product (**see Box 1**). The Marcus equation had fairly good success in describing ET reactions in organic and organometallic materials, a classic example being in $S_N2$ (bimolecular nucleophilic substitution) reactions [4, 5]. Measurements on such reactions primarily utilizing optical spectroscopy techniques have allowed one to directly verify the Franck-Condon term and obtain internal the reorganizational energy[5]. However, the description of these terms becomes intractable with the size of the reactant molecules, the solvation dynamics, and the excitation mechanism of reaction. In a pump-probe study of reaction dynamics, the system is usually excited by an ultrafast optical pump pulse (typically a few femtoseconds wide). The pump pulse will initiate non-equilibrium dynamical effects involving nuclear motions of the reactants and the solvent. The actual reorganization of electrons in such experiments is vague due to the lack of the information on transient structures of excited state and charge separated state.

The solvent ions will relax after the excitation processes, leading to inertial motion (typically ~10 fs) and slower diffusional relaxation (~500 fs - many ps) of ions in the solvent, reactant, and product at ambient temperatures.

At low temperatures the ET reaction may proceed via quantum mechanical tunneling [6]. In addition, the non-equilibrium state produced by the pump pulse will also generate coherent intramolecular vibrational excitations of reactants and product. The influence of coherent vibrational effects on ET reaction is at the forefront of photosynthetic reactions. The visualization of the coherent vibrational motions leading to the TS will transform our understanding of chemistry by providing information about the displacement pathways of all of the atoms involved.

If the atomic motions are directly mapped along the reaction trajectory with an ultimate time resolution, the most fundamental information embedded in the potential energy surfaces defining TS can be measured. Toward this goal, an x-ray molecular movie is needed with (1) a time resolution that is sufficient to resolve the atomic motions with (2) a frame rate that is comparable to inertial motion or the stretching frequency of the reactants and shorter than the diffusive relaxation times. Time-resolved x-ray spectroscopy or diffraction techniques would be suitable for this purpose provided the canonical x-ray shutter open-time (or pulse width) in these experiments is ~50 fs and one could open the shutter repeatedly along the reaction path of about 100 ps. Experimentally these were impossible requirements a few years ago, but with the newly developed x-ray free-electron laser technology the future is bright. Such molecular movies will address some of the fundamental questions that have remained unanswered:

a) What is the time sequence of molecular fragmentation or association in terms of electron density shift and nuclear geometry change?
b) What are the structural origins for the solvent effect?
c) What are the actual vibrational motions are involved in the transition state?

With that level of insight, it is hoped that the workings of artificial photosynthetic systems for solar fuel cell or electricity generation can be unraveled.

The x-ray free-electron laser (XFEL) sources provide either monochromatic or pseudo-monochromatic beams of hard x-rays suitable for time-domain diffraction studies of structures, although no one has yet mastered the continuous energy tunability of the x-ray beams often required for spectroscopy experiments. At the time of this workshop, the Linear Coherent Light Source (LCLS) at Stanford Linear Accelerator Center (SLAC) has been operating for about two years delivering x-rays with a bandwidth of ~45 eV, intrinsically determined by the lasing process, namely self-amplified-spontaneous-emission (SASE). This is the first such x-ray source that generates ~50-fs x-ray pulses with a pulse rate of 120 Hz suitable to measure simultaneously the dynamics of electronic distribution and nuclear geometry changes. Three more XFEL sources with slightly differing pulse-rate characteristics are on the horizon in Japan, Germany, and Switzerland. To make a molecular movie of a chemical reaction, the x-ray pulse from these sources will provide enough 8-10-keV x-ray flux to essentially capture structures at the atomic level in a single shot.

# Box 1: Control of Electron Transfer in Photochemical Reactions: Marcus Non-Equilibrium Free Energy Theory

*Many photochemical reactions are associated with electron transfer, in which an electron moves from a donor (D) chemical species to an acceptor (A) chemical species under the excitation of light. Photosynthesis in nature is a perfect example. The early work on electron transfer phenomena was highlighted by the Nobel Prize in Chemistry awarded to Rudolph A. Marcus. He pointed out that the electron transfer rate, $k_{ET}$, given by the Golden Rule, is governed by three important factors:*

*1. The driving force (activation energy) $\Delta G_0$*

*2. The reorganization energy $\lambda$, related to the electronic Hamiltonian coupling*
          *$<\psi_e(A)|H|\psi_e(D)>$*

*3. The electronic coupling strength $|H_{DA}|$, the Frank-Condon term, governed by the overlap of vibrational wave-function overlap $<\phi_N(A)|\phi_N(D)>$*

**Marcus Equation**

$$k_{ET} \propto |H_{DA}|^2 \exp[-\frac{(\Delta G_0 + \lambda)^2}{4\lambda k_B T}]$$

"The dominant challenge in ET kinetics is gaining a detailed understanding of how the dynamics (rate constants and barriers) for ET reactions are determined by the molecular and electronic structures of the reactants, the nature of the interaction between them, how the initial states are prepared, and the overall energetics." —Barbara, Meyer & Ratner, 1996

Direct structural information resolves:

- The transition state structure for the charge separation and how to control the rate and the yield of the ET;
- Active vibrational modes for the ET;
- Charge distribution coupled geometry changes;
- Solvent/environment structures (solvation);

Control ET reaction via structural factors.

*R.A. Marcus, On the theory of oxidation–reduction reactions involving electron transfer I, J. Chem. Phys. **24**, 966 (1956); R.A. Marcus, N. Sutin, Electron transfers in chemistry and biology, Biochim. Biophys. Acta Bioenerg. 811, 265–322 (1985).P. F. Barbara, T. J. Meyer, and M. A. Ratner, Contemporary Issues in Electron Transfer Research, J. Phys. Chem. **100**, 13148 (1996)*

The repetition rate of such pulses from these sources is too limited to shoot a true movie with the required frame-rate. All the above mentioned XFELs provide 10-120-Hz rate, but the Euro-XFEL in Germany will deliver considerably higher rate (~5 MHz).

In the next section, a brief summary of time-domain x-ray structural work performed utilizing presently available third-generation storage-ring based sources will be presented.

### 6.2.1 Understanding Reaction Dynamics in Solar Cells

In this section the focus will be on non-equilibrium photochemical reactions that are critical to our understanding of energy conversion, photosynthesis, and catalytic processes. An excellent example for understanding the importance of chemical reaction intermediates is a dye-sensitized solar cell (DSSC), schematically shown in Fig. 6.2 [7].
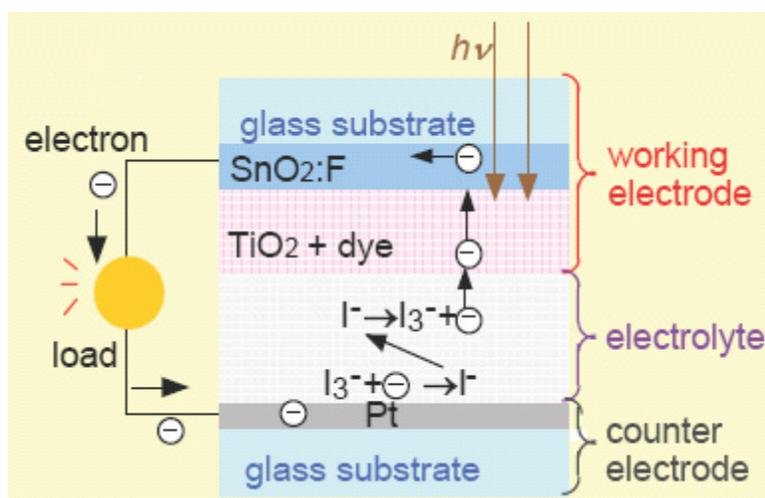


*Figure 6.2 Schematic representation of the principle of a dye-sensitized solar cell. Source: Michael Graetzel, Swiss Federal Institute of Technology, Lausanne.*

At the heart of a DSSC is a mesoporous oxide layer composed of nanometer-sized particles of $TiO_2$ (anatase) to which a monolayer of the charge transfer dye is attached. A fluorinated $SnO_2$ layer acts as a conducting transparent electrode. Photoexcitation of the dye (typically a chromophore such as ruthenium (II) tris-2,2'-bipyridine) results in the injection of an electron into the conduction band of the anatase. Electron donation from the electrolyte brings the dye to its ground state. The electrolyte is usually an organic solvent containing a redox system, such as the iodide/triiodide couple. The iodide is regenerated in turn by the reduction of triiodide at the counter-electrode in the cell.

The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. This is a perfect energy conversion process that has an efficiency of about 10-11%, and no long term chemical transformation.

It is equally important to address the times involved in various chemical processes in a DSSC. Photons (~ 720 nm or 1.72 eV) are absorbed by the dye molecules, which then are excited. The excited dye injects an electron into the nanocrystalline $TiO_2$ material. This process is extremely fast and takes only pico- or femtoseconds. The electrons are transported through the $TiO_2$ to the $SnO_2$:F electrode. The dye molecules are left in an oxidized state and reach the ground state through the redox capture of the electrons (see Fig. 6.3). The electron migration across the nanocrystalline film may take hundreds of nanoseconds to milliseconds.
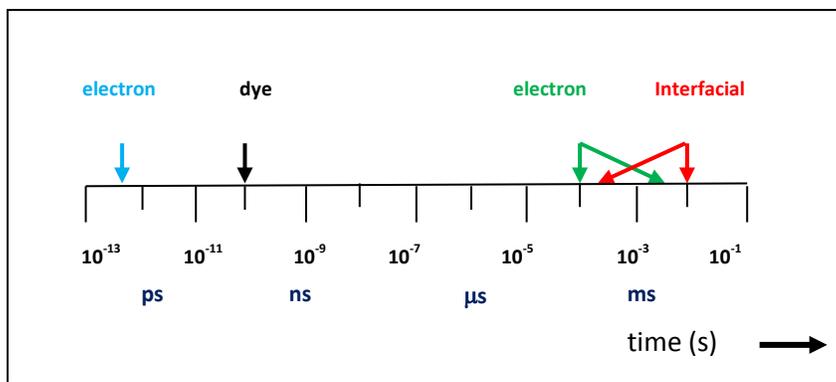


*Figure 6.3  Dynamics of redox processes involved in the conversion of light to electric power by dye-sensitized solar cells [8].*

The dynamics is determined by the design of the DSSC in which it is possible to make the dye molecule optimal for absorption of light and the charge transport materials, $TiO_2$, optimal for charge transport. The dimensions of nanoparticle provides most favorable exposure to solar light and gives a larger freedom in design of the most effective material combination. The energies of the electronic levels should also be favorable for a high voltage operation of the cell. For example, the lowest unoccupied molecular orbital (LUMO) level of the dye should be close to the conduction band of $TiO_2$ and the highest occupied molecular orbital (HOMO) level of the hole-conductor should be close to the HOMO-level of the dye (Fig. 6.2). In this way, the highest possible voltage from the cell can be obtained. Thus, the design freedom also dictates the electron dynamics, which ultimately influences the conversion efficiency.

The type of metal-to-ligand charge-transfer (MLCT) processes forming chemical transition states discussed above occur in a large class of systems from small molecules to large metalloproteins, and in applications such as tandem devices for direct cleavage of water into hydrogen and oxygen by visible light. Although kinetics, energetics, and coherence of photoexcited molecules have been revealed by ultrafast laser spectroscopy, structures of these molecules in their photoexcited or transition states have only recently been explored with the availability of third-generation x-ray sources. In general, x-ray absorption spectroscopy techniques such as x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS), and ultrafast scattering techniques (wide-angle scattering, WAXS) are ideal tools for studying the chemical and geometrical structures of laser-excited intermediate

(or transient) states. The third-generation synchrotron sources such as the APS deliver fast and intense x-ray beams to probe transients living 100 ps or longer.

Early examples of the laser-pump x-ray probe measurements employed to understand the formation of excited and intermediate states were the investigation of ruthenium (II) tris-2,2'-bipyridine $[Ru^{II}(bpy)_3]^2$ [9] and NiTPP-L2 (NiTPP, nickeltetraphenylporphyrin; L, piperidine) [10], both of which are considered model dyes in solar cells. The XANES measurements established the existence of the 300-ps intermediate triplet state in the Ru-bpy compound, and confirmed that the photoexcitation leads to a rapid removal of both axial ligands to produce a transient square-planar intermediate in NiTPP with a lifetime of 28 nsec. The transient structure of the photodissociated intermediate is nearly identical to that of the ground state NiTPP, suggesting that the intermediate adopts the same structure as the ground state in a non-coordinating solvent before it recombines with two ligands to form the more stable, octahedrally coordinated NiTPP-L2.

In spite of efficient performance of Ru-complexes in solar cells, the price of Ru is too high to be of commercial viability in the long run. Hence, alternative complexes have been considered. One of the promising dyes is based on $[Cu(I)(dmp)_2]^+$ complexes . The metal-to-ligand-charge-transfer excited state of $[Cu(I)(dmp)_2]^+$ $(3d^{10})$ complexes can be created by visible photons that shift one electron from Cu(I) to the ligand, forming a transient Cu(II) $(3d^9)$ [11]. This transition is analogous to the dye sensitizer Ru(II) complexes. The excitation triggers a Jahn-Teller distortion from a ground-state tetrahedral Cu(I) to a transition state with a penta- or hexacoordinated Cu(II) geometry, which is the structural basis for molecular rotors and shuttles. Therefore, these Cu(I) complexes are excellent candidates for replacing precious metal complexes in DSSC and have been a core functioning group in molecular machines. Previous x-ray transient absorption spectroscopic studies revealed an exciplex (or an excited molecular entity made with a ground state counterpart of a different structure) formed between the MLCT state and a solvent molecule as a ligand; and the ultrafast optical spectroscopic studies suggested three time constants (Figure 6.4) of <500 fs, 10-ps and 1-100 ns for the excited state formation and decay kinetics [11].

The observed first sub-picosecond component has been assigned to the trahedral flattening of the molecule, but when the flattening exactly does occurs relative to the photoexcitation is unclear [12]. Such an ambiguity persists because the optical signals for the exciplex or ligated species are unknown and overlay with each other.
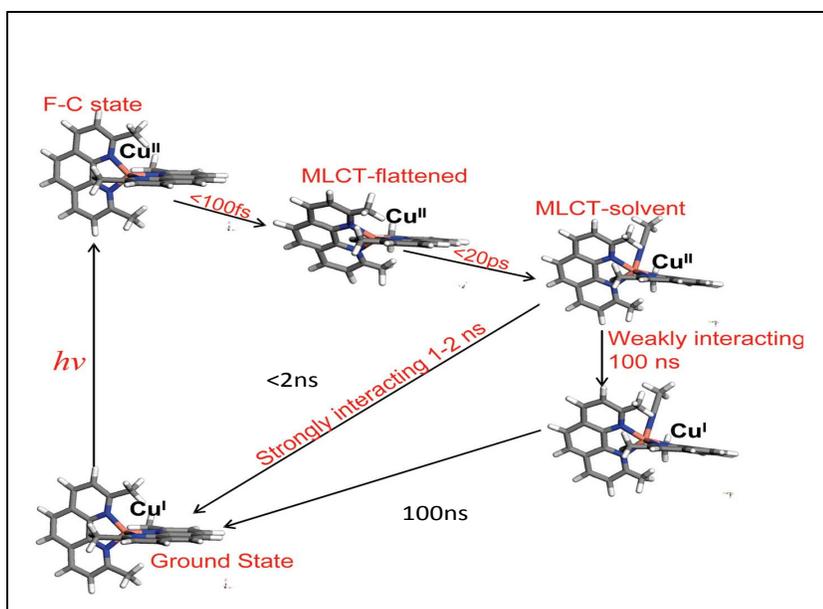
*Figure 6.4  The excited state structural changes and associated time constants from previous studies on [Cu(I)(dmp)$_2$]$^+$ [11].*

Utilizing the x-ray source energy of 8986 eV (corresponding to the 1s to 4p$_z$ transition in Cu(I)) from LCLS with a 70-fs time resolution, the Cu coordination state change reflecting the flattened MLCT state and exciplex ligation could be detected.

The current literature presents two different views on correlations of structures and MLCT excited state lifetimes, one of which suggests that a flattened geometry could prolong the excited state lifetime, and that a rigid tetrahedral geometry would sustain a long excited state lifetime. There are several Cu(I) phenanthroline complexes with different starting dihedral angles of the two ligands and varying constraints and sizes. The suggested investigation utilizing the LCLS and a few-eV energy resolution to cover the sharp feature at the rising edge of Cu K transition will provide knowledge about the correlation between the structure and excited state kinetics and will suggest molecular designs for a long-lived excited state for electron injection in DSSC and fast movements in molecular machines.

A number of photoexcited molecular structural studies have now been performed, including excited state metalloporphyrins and their structural changes in photocatalytic reactions, metal-to-ligand-charge-transfer excitation of transition metal complexes, and triplet state formation of organometallic building blocks [3]. These studies aim at capturing the transient molecular structures that are crucial to the outcome of the photochemical reactions, such as the correlation of reorganization energy of the excited states with their lifetimes in photoinduced charge separation. Combining results from excited state structural studies with those from ultrafast optical studies and a combination of computational strategies and techniques such as Time Dependent Density Functional Theory (TDDFT), Car–Parrinello molecular dynamics simulation, continuum salvation models, etc. would give new insight into the photochemical pathways and provide guidance in synthesizing molecules with targeted functions.

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Future prospective with much shorter x-ray pulses with XFELs (e.g., LCLS) and ERLs and utilizing XAFS and WAXS will deliver the fundamental knowledge require for optimal design of photovoltaic cells of the future.

## 6.2.2 Solvation Dynamics

The chemistry in the solution phase has formed an important field of research because many chemical and biological reactions take place in a solution. The major challenge in understanding solution-phase chemistry arises from the presence of numerous solvent molecules surrounding a solute molecule, leading to solute–solvent interactions. The native environments often alter the rates, pathways and branching ratios of chemical reactions through various effects such as cage formation, isomerization, ring closure, dimerization, dissociation, recombination and diffusion. The solvation photochemistry is even more complex and it is crucial to consider the complex effects of solvent molecules on the reaction energetics and dynamics (the solvation effect). While the early work on photoexcited reactions in solution used XAS technique [13], the time-resolved x-ray scattering and diffraction have been successfully employed in recent years [14, 15] to map the reaction path. In an x-ray scattering experiment, the changes in the scattering signal is composed of three time-resoled effects:

(1) A solute only term arising from the internal structure of the solute

(2) A solute–solvent cross term (or the solvation cage term) reflecting the organization of solvent molecules around the solute

(3) A solvent-only term reflecting the bulk solvent structure, all of which may also display time-resolved effects

The last term reflects the temperature and density changes in the solvent from the laser pump pulse.

Two examples were highlighted in the focus team discussions. The molecule of tetrakis-µ-pyrophosphitodiplatinate(II) $(Pt_2(P_2O_5H_2)_4^{4-,}$ PtPOP), with a square planar geometry around two Pt atoms, in aqueous solution was considered a prototype for fully developing x-ray scattering technique to understand the photochemistry. Figure 6.5 a. contains the structure of the molecule and its electronic excited states.

Detailed x-ray scattering work [16] on a time scale from 100 ps to 1 $\mu$s after laser pu the data shown in Figure 6.5 b. The measured x-ray difference-scattering intensities, Q. $\Delta S(Q)$, shows the solvation dynamics following the pump pulse. The interpretation of the data establishes the technique as a viable tool to uncover details on the formation of a binuclear exciplex and its solvation products. Further progress in the field, especially for a full understanding of the exciplex state dynamics in polynuclear metal complexes requires strong theory support.

The early results discussed at the workshop on the understanding the x-ray difference-scattering data measured following the photo-initiated synthesis forming the lowest triplet exciplex states and comparing them with time-dependent density-functional-theory (TD-DFT) calculations on polynuclear TlPtPOP and AgPtPOP are very encouraging [17]. The molecular structure of the complexes and the measured data (Figure 6.6) when compared to gas phase calculations showed that the surrounding solvent has an important role to shorten the Pt–Pt and M–Pt (M = Ag, Tl) bond lengths, lowering the

molecular orbital energies. This influences the molecular orbital transitions upon excitation and stabilizes the excited transient molecules in solution. The TD-DFT calculations predict double exciplexes, such as M-PtPOP-M (M = Ag, Tl). The question remains whether such transition states are observable in the x-ray scattering measurements.
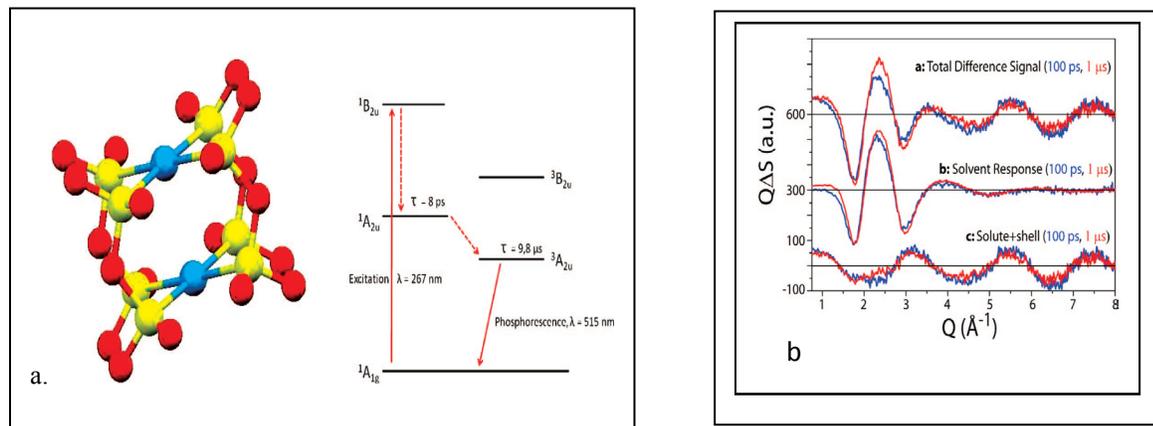


*Figure 6.5  a.  Model structure of the PtPOP anion,  without hydrogen atoms (Pt, blue; P, yellow; O, red). (right) Electronic states of PtPOP. b. (top) Total difference signal, 100 ps (blue) and 1 μs (red), after optical excitation of 12 mM $K_4PtPOP$ in water obtained by subtracting the average light-on scattering signal from the correspondingly averaged light-off signal. (middle) Bulk-solvent difference-signal response as modeled for the two time delays. (bottom) Solute + solvent cage signals [16]*

Over the past decade iron pentacarbonyl, $Fe(CO)_5$, has become the poster child of photochemistry investigations in gas phase and in solution. There is a wealth of data from optical spectroscopy and electron diffraction pump-probe measurements on the photoreaction path in this compound following excitation by ultraviolet light. The main findings were the loss of one or more CO ligands and subsequent formation of coordinatively unsaturated carbonyl complexes, which are known to catalyze a variety of reactions [18,19].

The solvation dynamics following photo excitation intimately depended on the solvent. In alcohols, the interaction is primarily between the electrons of the hydroxyl-oxygen of the alcohol and one of the carbonyl-carbons in $Fe(CO)_5$. In fact, mainly the complex $Fe(CO)_5$–EtOH is formed when pentacarbonyl is added to alcohol.

It is expected that photo excitation of this complex does not have to proceed through a dissociative process followed by a diffusive encounter of the reaction intermediate with a solvent molecule unlike that observed in gas phase. The situation might hence lend itself to the study of coherent control of interactions from the reactants to product. An anticipated signature would be the absence of the intermediate $Fe(CO)_4$ and a triplet state. The optical work utilizing a UV-pump and transient IR-absorption (TIR) probe spectroscopy has not shed light on this due to limited temporal resolution of several picoseconds [20]. Are the x-ray spectroscopy time domain measurements have more power? Should one be concerned about the intensity of x-ray probe pulse leading to fragmentation?
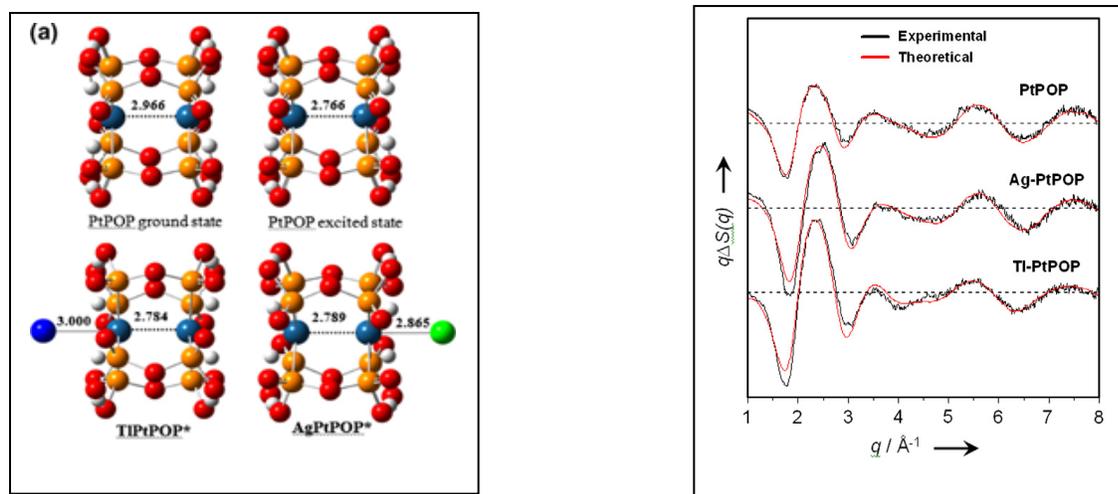
*Figure 6.6  Molecular structures and their x-ray difference-scattering signatures q$\Delta$S(q).  (a) TD-DFT optimized molecular structures of PtPOP in the ground and lowest triplet excited states and the exciplexes Tl-PtPOP\* and Ag-PtPOP\* in aqueous solution. Pt, P, O, Tl, Ag and H atoms are colored in cyan, orange, red, blue, green and gray, respectively. (b) Experimental x-ray difference-scattering intensities q$\Delta$S(q) of PtPOP, Ag-PtPOP and Tl-PtPOP in aqueous solution (from top to bottom, black curves), and the comparison with a theoretical model (red curves) of the solute signals. To make a direct comparison, the DFT calculated structures were compared with the experimental data without further optimization of the structural parameters [17].*

The ultrafast XANES data with picosecond time resolution [21] indicate that CO ligands can be rapidly substituted with an incoming alcohol after photo excitation of solvated $Fe(CO)_5$ in ethanol. Further understanding requires higher time resolution (~50 fs) x-ray absorption and scattering data (perhaps utilizing an XFEL), in particular to distinguish between various reaction paths involving vibrationally hot $Fe(CO)_5$ and $Fe(CO)_4$–EtOH.

### 6.2.3  Information Storage

The family of compounds that has attracted much attention because of their potential use for information (memory) storage is the solvated 3d and 4d transition metal complexes that show photo excited spin cross-over phenomena. In these systems the emphasis is on tracking the charge, spin, and covalent interaction between the metal, ligands and solvation molecules to gain a mechanistic understanding of de-excitation in coordination chemistry. While femtosecond-resolution optical spectroscopy can accurately determine the kinetics and time scales of the relaxation, such spectroscopy cannot directly determine these key degrees of freedom, and consequently does not allow accurate determination of the reaction mechanism. On the other hand the measured x-ray movies of the processes associated with the spin switching from photo excitation provide vital knowledge on the interplay and coupling between the nuclear, electronic and spin degrees of freedom (low-spin to high-spin transitions).

The photo switching of spin states in spin cross-over molecule Fe(II) bipyridine in aqueous solution is a model compound that has been extensively investigated since it resembles oxygenation of myoglobin to hemoglobin. The bipyridine molecule shows unusually fast intersystem crossings between low- and high-spin states, possibly involving non-Born-Oppenheimer dynamics. Similar Ru, Co, Ni molecules along with binuclear systems such as Ru-Co and Fe-Nb charge transfer molecules have also been extensively investigated utilizing the x-ray tools. While time-domain x-ray absorption spectroscopy (XAS) and x-ray difference scattering discussed earlier are the most popular probe techniques, in recent year x-ray emission spectroscopy (XES), x-ray diffuse scattering (XDS) and resonant inelastic x-ray scattering (RIXS) have gained much more relevance with regard to the phenomena to be probed. The combination of these tools will allow disentangling the sequence of events leading to the product state in spin-cross over reactions.

In the prototype bipyridine is $[Fe(tren(py)_3)]^{2+}$, a spin crossover complex, a low-spin ($^1A_{1g}$) ground state (S=0) undergoes ultrafast spin-state conversion to a high-spin ($^5T_{2g}$) state (S=2) upon excitation into a singlet metal-to-ligand charge-transfer state (1MLCT, λmax = 560 nm). In the pump-probe studies of this complex [22] in a $CH_3CN$ solution x-ray absorption was measured utilizing Fe $L_3$-edge following the photo excitation. The spectrum can distinguish between the ground low-spin state at 709.4 eV and the transient excited high-spin state at 707.6 eV. This allows one to measure the lifetime of the high-spin state to be 60 ns for this system. The details of this measurement are shown in Figure 6.7.

The same phenomenon of spin crossover can be directly detected utilizing XES as shown in Figure 6.8 [23]. The measurements performed on aqueous [Fe(bpy)3]2+ molecules 60 ps after an ultrafast laser pulse excitation are compered to theory calculations. 1s x-ray emission spectroscopy (XES) represents a direct probe of the spin state of 3d transition metals, due to the exchange interaction of the core hole with the 3d electrons in the final state. The intensity of $K_\alpha$ emission lines provides information on the number of unpaired electrons.

Both the x-ray absorption and the emission spectroscopy investigations have not shed much light on the effect of solvation due to intrinsic time resolution limits of the measurement ~ 200 fs. A systematic solvent study with <50 fs time resolution utilizing XFEL sources could aid in clarifying the role of the solvent in these excited-state dynamics. The theoretical calculations of the solvation dynamics predict observable changes in the measured absorption, difference scattering and emission spectra [24].

The early events in a photocatalytic active bi-metallic bipyridine-based Ru-Co compound have been recently measured, where several TSs exist during i) photoinduced Ru to Co charge transfer, which leads to ii) a reduction of the Co ion, which partially undergoes a iii) spin transition. Since XES tools are sensitive to spin changes in the central atom, both the charge transfer as well as the spin conversion can be monitored on the femtosecond time scale. Simultaneous XDS will identify the nuclear motion, especially between both Ru and Co atoms. Since both XES and XDS deliver complementary information, their combination in a simultaneous measurement will allow us to unravel the interplay between nuclear movements and electronic interactions. At the time of the workshop, the experiments performed with 100 fs resolution LCLS were being analyzed [25].

We believe that the first determinations of transition state structures in isomerization reactions will be a paradigm changer. Continuation of such measurements in a thematic program to determine transition state structures in many reactions will yield a data-base that can be used to suggest new concepts and to test old concepts *vis a vis* the relationships between structure and reaction mechanism; the results of such data mining are likely to greatly advance our understanding of chemical reaction pathways.
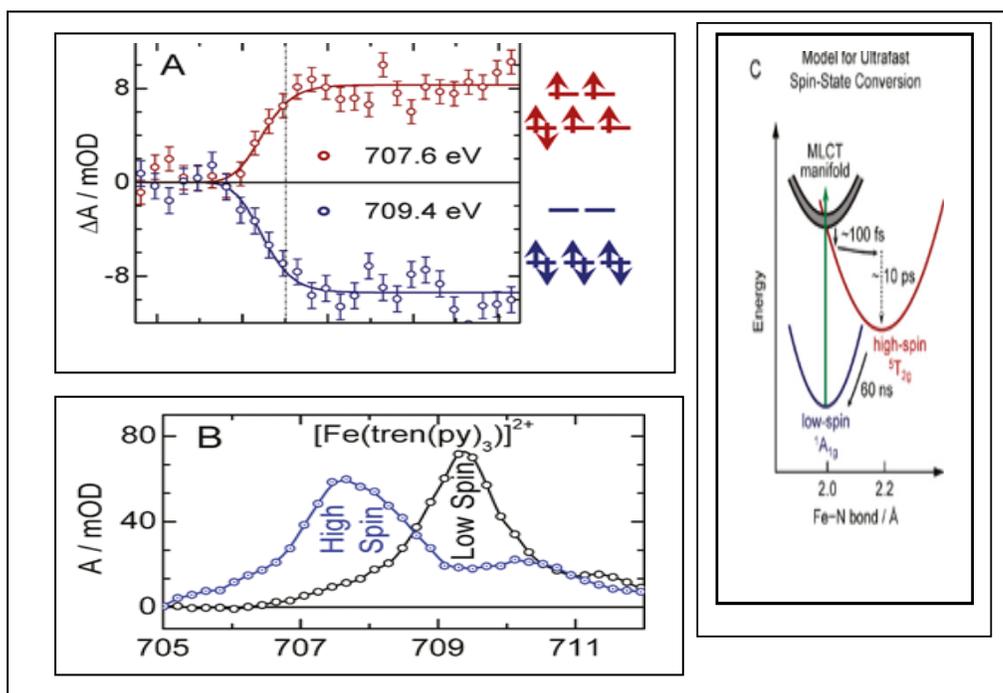


*Figure 6.7  A. The changes in the L3-edge intensity measured at the location of low-spin (blue) and high-spin (red) states (see B) after populating the MLCT manifold shown in C. The resulting lifetime of the high-spin state is 60 ns [22]*

*Figure 6.8 a) Energy scheme for $K_\alpha$ emission in $Fe^{2+}$ described in Fig. 6.7 C. b) Calculated $K_\alpha$ fluorescence lines for HS (thin line) and LS (thick line) $Fe^{2+}$ in an octahedral crystal field. The difference spectrum is also shown (dashed line). c) Experimental Ka spectra of HS and LS $Fe^{2+}$ reference compounds ([Fe(phen)$_2$(NCS)$_2$] and [Fe-(bpy)$_3$]Cl$_2$ powders, respectively) [23]*
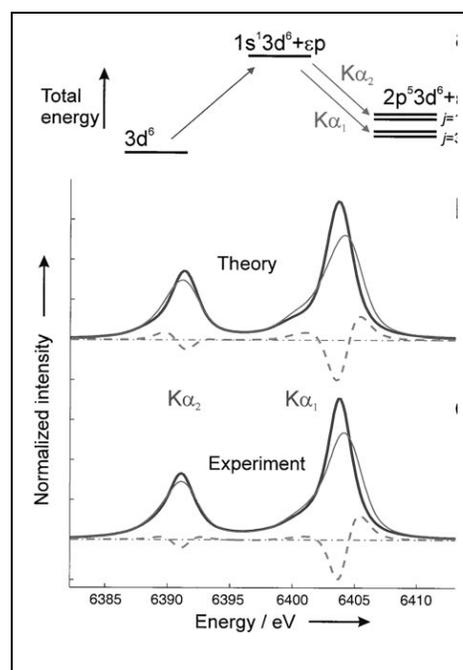
The information concerning TS structures in chemical reaction pathways can only be captured when the time-resolution of the structural method is comparable to the vibrational period for the modes that are responsible for the bond breaking and formation, as well as isomerization. The TS structures will tell us how molecules cross the potential barriers and the possible ways to manipulate reaction pathways coherently and incoherently through external forces and chemical modification.

## 6.3 Quantum Control of Chemical Reactions

One of the intriguing aspects of understanding chemical reaction dynamics is the possibility of utilizing this knowledge to control the outcome of chemical reactions. The practical reasons for seeking such control of a chemical reaction range from suppressing unwanted side products to synthesizing new structures, nanoengines, and new materials. Successful control is commonly practiced by a variety of means, such as varying the external conditions of the reaction mixture by changing, for example, the temperature or pressure or the redox potentials, or finding a suitable catalyst that selectively lowers the activation barrier to the desired reaction products. Control of chemical reactions utilizing laser fields is a well-established concept in simple systems and in femtochemistry [26]. There have even been attempts at vibrationally mediated photoreactions **(see Box 2).**

### 6.3.1 Few Candidate Examples

Several strategies have been tested over the years to photoexcite and intervene in the transition states. Coherent control methods exploit a number of constructive and destructive interferences that can be manipulated to obtain a desired outcome. For example, the pump pulses can be variably shaped in space and time to selectively perform desired molecular excitation in the gas and liquid phase or on the surfaces [27].

# Box 2:
## Examples of Coherent Control of Gas Phase Reactions Using Shaped Ultrashort Optical Pulses



$CO_2$    $CCl_4$    Shaped Pulse    $CCl_2O$
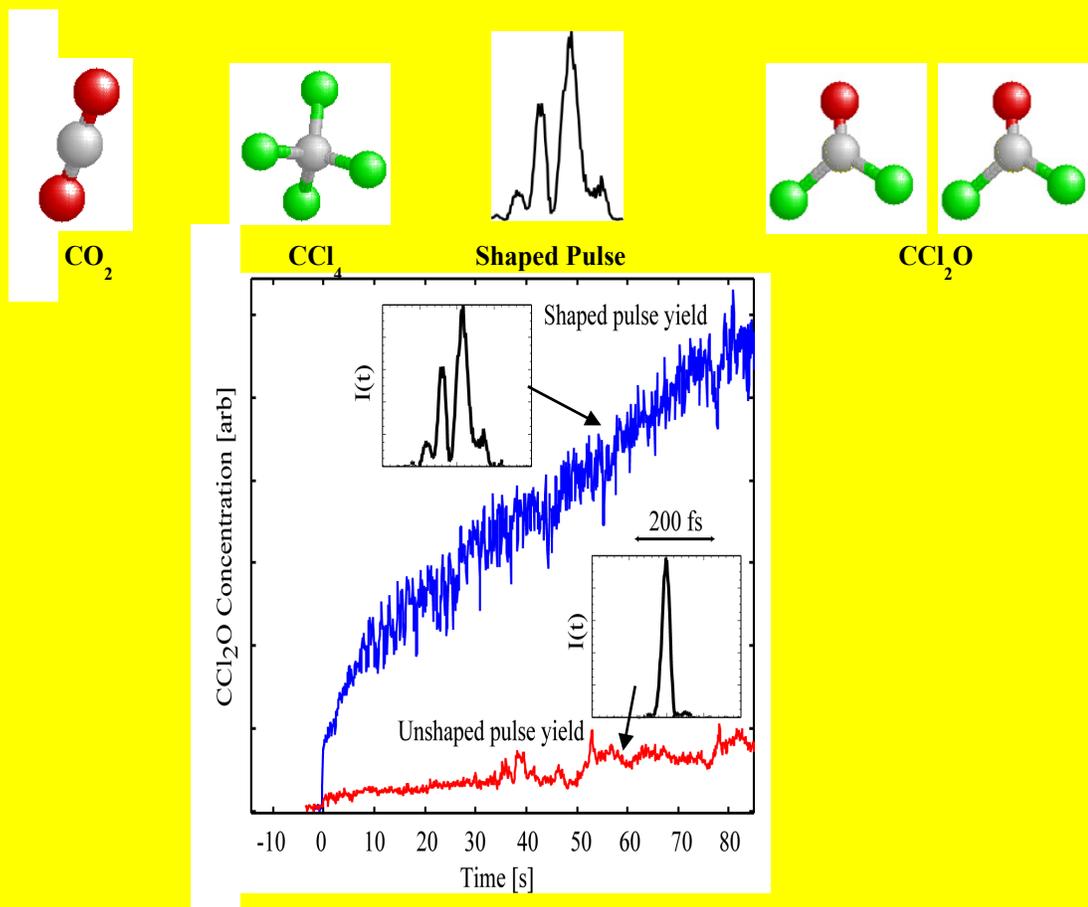
*Extensions to complex molecules will require the use of modern laser technology that allows sculpting of the phase, amplitude and polarization of laser fields in the infrared, optical, ultraviolet, and in future, x-ray spectral regimes. Combining this technology with intelligent feedback based on x-ray tools will be essential for coherent control of complex systems, such as the large molecules in the solution phase.*

This will provide considerable knowledge on the linear and nonlinear chemical pathways in a chemical reaction through optimally controlling the phase and amplitude of the pulse [28]. Shaping of all aspects of the THz fields - the amplitude, phase, and polarization profiles - can contribute substantially to coherent control over collective material dynamics and structure as the simulations demonstrate in PbTiO$_3$ [29]. The optimization algorithms to realize one set of chemical products over another have been developed. For example, selective excitation of one specific molecule in preference to another within liquid-phase solute/solvent mixtures containing [Ru(dpb)$_3$]$^{2+}$ has been demonstrated utilizing two coherent laser light fields [30]. In coherent control experiments, the shaped laser-pulse can also suppress unwanted chemical pathways, as well as increase or decrease the absolute quantum yield of a chemical reaction. While intense laser fields have been utilized in many experiments to control the excited-state population, the intensities relevant to the processes in nature can control the reaction coordinates, thus mimicking nature.

What would be the role of ultrafast x-ray probes in understanding the role of control filters in a chemical reaction? While ultrafast optical spectroscopies provide the ability to probe changes in energy levels with femtosecond time resolution, these methods yield indirect information on molecular structure. Probes of vibrational modes can provide more direct information on molecular structure, but are complicated by interference from absorption of the surrounding medium. In contrast, x-ray spectroscopies, XANES and XAFS, have the potential to provide direct structural information with atomic specificity and can be used to study molecules in complex fluid environments including liquids and proteins. Ultrashort x-ray pulses will also provide an unparalleled tool for investigation of molecular structure on the time scale of chemical reactions. The ~100 ps x-ray pulses currently available at the storage-ring sources allow investigation of metastable intermediate states in relaxed local environments. Pump-probe measurements with even < 1 ps x-ray pulses will enable investigation of molecules as they react, following both the initial molecular rearrangements and the subsequent relaxation and solvation. In schemes to control molecular dynamics in the solution phase, typically the feedback schemes have utilized visible fluorescence or strong infrared pulses following the control pulse from an optical laser. Each of these feedback variables has its limitations. One may envision the ultrafast x-ray pulses to provide a more incisive and direct probe of electronic dynamics and thus a more general feedback scheme.

Single-shot, near-edge x-ray absorption, emission and inelastic scattering spectra on ultrafast timescales, appropriately synchronized to the initial controlled excitation, could be a novel and versatile feedback mechanism for quantum control in complex systems.

An important example is the photoreactions of alkylhalides in solution which provides a protype system with relatively simple spectroscopic features but complex condensed phase reaction dynamics. The photochemical reactions of iodohalomethanes including bromoiodomethane have been associated with the production of volatile organic iodine compounds contributing to the ozone depletion cycle [31]. Relevant photochemical processes occur both in the gas phase and in aqueous solution. Excitation of CH$_2$BrI at 266 nm results in rapid cleavage of the C-I bond forming iso-CH$_2$Br—I (Figure 6.9) [32,33]. Formation of the isomer is complete within a few picoseconds, with relaxation and solvation occurring on time scales of 10-40 ps depending on the solvent. The UV-visible signatures of the intermediate

species are broad, structureless, and possess ambiguous assignments. Carbon-halogen and halogen-halogen vibrational bands are at relatively low frequency, outside of the range easily accessible for sophisticated transient IR measurements and complicated by IR absorption of the surrounding solvent. Time-resolved liquid-phase x-ray diffraction method is powerful in addressing the dissociation of molecules such as iodohaloethanes dissolved in polar solutions [34]. A transient intermediate has long been hypothesized to explain stereochemical control in many association and/or dissociation reactions involving haloalkanes. Ultrashort optical pulses were used to dissociate an iodine atom from the haloethane molecule ($C_2H_4I_2$) dissolved in methanol, and the diffraction of picosecond x-ray pulses from a synchrotron supports the following structural dynamics, with 0.01 angstrom spatial resolution and 100 picosecond time resolution: The loss of one iodine atom from $C_2H_4I_2$ leads to the C-I-C triangular geometry of $CH_2ICH_2I$.

Time-resolved XANES and EXAFS will allow direct monitoring of changes to the halogen environment due to changes in bonding and solvation. Studies with ultrafast x-ray pulses will permit investigation of the formation of metastable complexes with halomethanes, differentiation of competing reaction channels, and observation of the solvation and relaxation stabilizing the product species
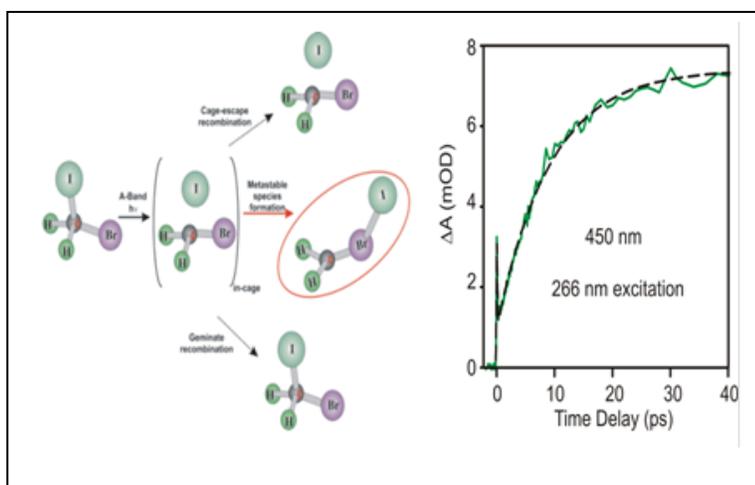


Figure 6.9  Proposed photofragment recombination reaction following excitation of CH2BrI. The optimized geometry of the observed iso-CH2Br-I species was calculated utilizing DFT [32]. Transient absorption measurements suggest that the quantum yield for the formation of the metastable species is high.

This transient then binds to an iodine atom to form a new species, the $C_2H_4I$-I isomer, which eventually decays into $C_2H_4 + I_2$. There are many events that precede the time resolution of these experiments in the femtosecond domain. For example, can we monitor the evolution of ultrafast reaction dynamics and motions of coherent vibrational wave packets in real time with are solution of femtosecond [35] utilizing XFEL sources? The photoreactions of cobalt containing corrins and corrinoids provide another system where pump-probe measurements with picosecond x-ray pulses will yield important insight into the electronic structure and dynamics of a key molecular chromophore. Vitamin $B_{12}$ is an essential human

nutrient, precursor to alkylcobalamins incorporated into the enzymes methylmalonyl Co-A mutase and methionine synthase (Figure 6.10). The photochemistry of the coenzymes and analogs has proven a useful tool in elucidating the electronic structure and reactivity of these compounds [36,37].
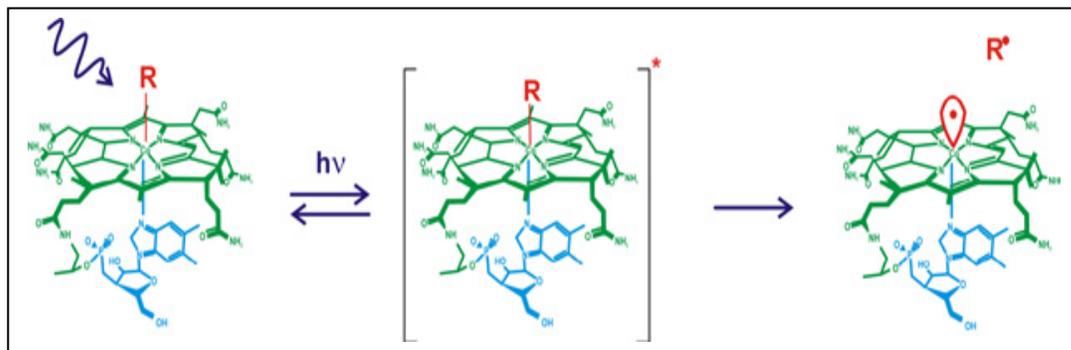


*Figure 6.10. Cartoon of the photochemical reactions of cobaltamins. The R group characterizes the different cobalamin species, CN in vitamin B12, CH3 in methylcobalamin, and 5' deoxyadenosyl in Coenzyme B12.*

Femtosecond to picosecond transient absorption spectroscopy has demonstrated the formation of an excited state species with an absorption spectrum and lifetime dependent on the nature of the upper axial ligand, R, the presence of the bottom axial ligand, and the nature of the solvent.

For the base-on compounds the lifetime of the excited state ranges from 1 ps in aquocobalamin (R=$H_2O$) to a 100 ps in coenzyme $B_{12}$ (R=5'-deoxyladenosyl) and 1 ns in methylcobalamin (R = $CH_3$). The absence of the axial nitrogenous ligand in the base-off cobalamins modifies the electronic structure and opens a channel for fast nonradiative decay [38]. This channel competes effectively with the channel for bond dissociation resulting in decay of the excited state on time scales of 10 to 50 ps.

UV-visible transient absorption measurements provide a signature of changes in the electronic state properties, but these spectra are broad and structureless reflecting the influence of the cobalt ligation on the $\pi$-$\pi$* transition of the corrin ring. Excitation of the adenosylcobalamin coenzyme in water, ethylene glycol and glutamate mutase results in distinctly different spectra for the lowest electronic excited state; the environment changes the electronic structure and state ordering [39]. The observed trends may be correlated with steady-state spectra as a function of oxidation state and ligation, but the assignments are speculative. Ultrafast XAFS and XANES measurements will permit direct measurement of the environment of the central cobalt atom as the molecule relaxes through the excited state manifold, permitting direct identification of the oxidation state of the cobalt and changes in the geometry of the surrounding ligands.

The two molecular systems sketched above provide examples of classes of reactions where ultrafast x-ray spectroscopy will provide important new information on the specific systems under investigation and increase the understanding of key condensed phase phenomena influencing reaction dynamics. In

both case the reactive species is well defined and the product quantum yield is near unity on the picosecond timescale. Many such well-defined problems may be identified. However, one significant drawback to the application of picosecond x-ray spectroscopies to the study of condensed phase molecular reactions arises from the presence of sample heterogeneity. In many cases samples of interest consist of a complex mixture of reactants differentiated by environment or conformation and/or the excitation pulse produces multiple products. In such cases it can be difficult to untangle the resulting signals. Optical pulse shaping provides a tool with the potential to select between alternative reactant species or to influence excited state reaction pathways [40]. Wavelength, energy, phase, beam profile, polarization, and temporal structure are all variable parameters in a light pulse. Control of these parameters has the potential to manipulate the light-matter interaction and to select from overlapping populations [26,41]. As such methods are developed they will allow extension of picosecond pump-probe x-ray measurements to a broader class of reaction, enabling the production of atomic level movies of molecules undergoing chemical transformation.

### 6.3.2 Coherent Spatial Alignment

Non-adiabatic alignment is a coherent approach to control over the spatial properties of molecules, wherein a short, moderately-intense laser pulse is applied to populate a broad rotational wave packet with fascinating properties. In the limit of small isolated molecules, non-adiabatic alignment has evolved in recent years into an active field of theoretical and experimental research with a rich variety of applications.

Our goal in future will be to extend the alignment concept to complex systems, including large polyatomic molecules, dissipative media, non-rigid systems, molecular assembly, and molecular junctions. Following a brief review of the essential physics underlying alignment, we consider the case of asymmetric top molecules, where alignment overcomes the mechanisms that render the rotations unstable in the classical limit. Molecular alignment can be extended to control the torsional motions of polyatomic molecules, and apply torsional control to manipulate charge transfer events in solutions, suggesting a potential route to light controlled molecular switches. In Figure 6.11 a simulation is presented. Turning to interfaces, a route to guided molecular assembly has been introduced, wherein laser alignment is extended to induce long-range orientational order in molecular layers [42]. Photo excitation of molecules in a condensed state populates rapidly decaying excited states and each state establishes changing electronic, vibrational, and structural (or geometrical) configurations. Each of the excited species has differing chemistry, generally referred to as photochemistry. The availability of x-ray pulses has provided unprecedented information on the structural origins of molecular properties in the excited states, as discussed earlier. In future, the time-resolution for the excited-state structure measurements utilizing ultrafast x-ray pulses should reach the femtosecond time scales, which will make molecular movies of bond breaking or formation and vibrational relaxation a reality. Laser-optimized femtochemistry in the gas phase and liquid phase can be improved by applying ultrashort coherent light fields in the wavelength range from the IR to the UV [43].
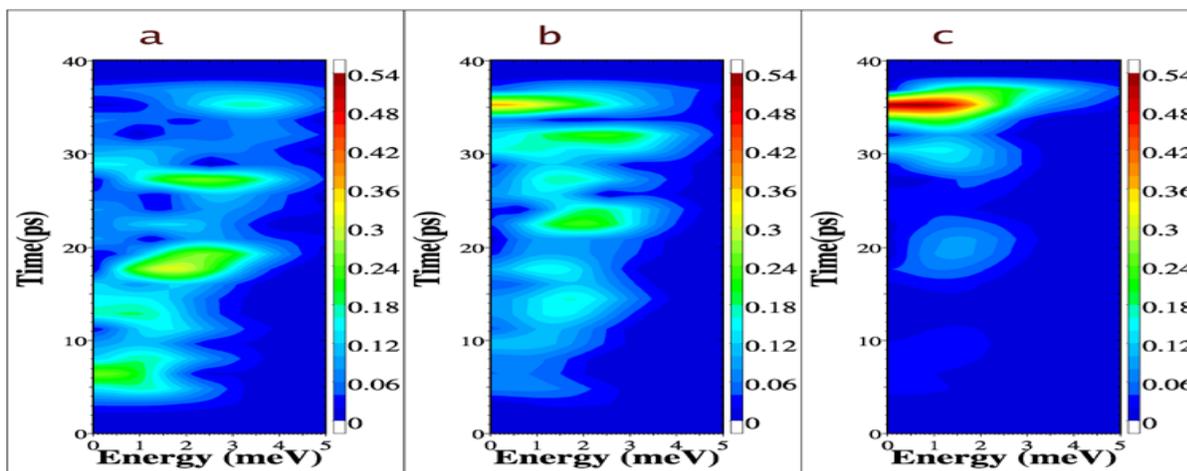
*Figure 6.11  Optimal control of alignment in a dissipative environment. Simulation of the optimal field vs time and energy plots for different pressures. As the pressure increases from a (0 torr), b  (100 torr), to c (200 torr), the alignment  mechanism changes, revealing details of the molecule-environment  interactions [42].*

## 6.4  Dynamic Propagation of the Reactions in Multiple Time and Spatial Scales

Light may direct the functionality of a material through spectacular photoinduced phenomena in the solid state. Due to cooperative interactions between constituents, the medium is active. Positive feedback can trigger the non-equilibrium transformation of the material towards another macroscopic state of different electronic and/or structural order, for instance from non-magnetic to magnetic or from insulator to conductor (see Section 4 of this report). Molecular materials constituted of multi-functional molecules which can be switched between two states by electronic excitation which are particularly promising. This is the focus of this panel where ultra-fast phase transformation develops after the material is prepared in an excited electronic state by an ultra-short light pulse. The advancement of this emerging field requires the mastering of three key aspects: light-induced coherent phenomena, intrinsic cooperativity in the material and new processes far away from equilibrium. This is illustrated in Fig 6.12.

X-ray scattering experiments have the potential to give a global picture of structural changes, at thermal equilibrium as well as out-of-equilibrium. Time-resolved diffraction experiments currently performed give fascinating potential not only to observe and understand the elementary dynamic processes in the material but also to watch how it can be directed to a desired outcome. Recent investigation of the structural dynamics in molecular materials by time-resolved x-ray diffraction with 100 ps time resolution on a synchrotron (ESRF and KEK) have allowed direct observation of the switching dynamics and has contributed to our understanding of the physical picture [44,45]. The key point is that in the solid state different degrees of freedom of different nature play their part on different time scales and the pathways are complex, from the molecular to material length and time scales.

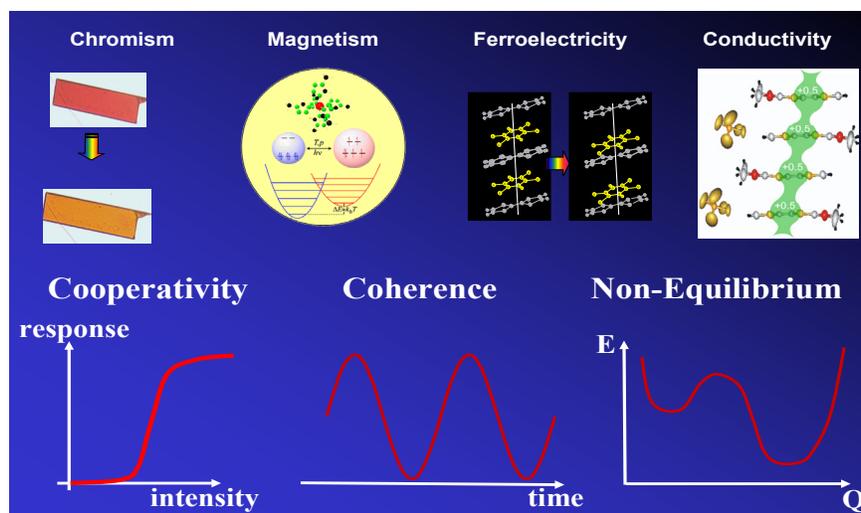*Figure 6.12  Key aspects of material transformation from photoinduced collective interactions in molecular materials. Courtes:  Herve Cailleau, University Rennes 1.*

Molecular materials constituted of multi-functional molecules which can be switched between two states by electronic excitation are particularly promising (see Figure 6.13). In the solid state photoactive molecules interact and this may be at the origin of fascinating collective and cooperative phenomena driven by an ultra-short laser pulse. The photoinduced transformation pathway is complex for such macroscopic system. A key point to be made is that the physics of coherent processes triggered by ultra-short laser pulse is different than thermal excitation and the dynamics is no more stochastic (as at thermal equilibrium), but instead deterministic. Controlling coherence is hence important since laser is not a mere heat source, instead it may coherently direct the system along the desired pathways on the potential energy surface. In addition, dynamical changes occur over different length and time scales through a sequence of processes, from molecular to material scale. The aim of photo-induced collective and/or cooperative phenomena in materials is to force the system towards a new macroscopic state far away from thermal equilibrium which is often beyond our current understanding of matter based on equilibrium dynamics. In fact, different subsystems of different quantum behavior, such as electrons, spins, phonons, molecular configurations, cell deformation, etc., play their part but on different time and length scales. Time-resolved x-ray diffraction offers fascinating capabilities not only to observe the elementary dynamical processes, but also to understand how material transforms and can be directed to a desired outcome.

This emerging field generates key questions, requiring new experiments and concepts to search for solutions of (a) how to control such complex transformation pathway from molecular to nanoscopic and finally material scale (see Fig. 6.13), (b) how to master ultrafast precursor structural dynamics such as coherent nucleation and oscillation coupled to functionality of the materials (c) what the limits on the speed of material switching are and (d) what impacts these ultrafast structural transformation could generate on future information and communication technologies, for instance in the ultrafast writing and reading of information.

In the context of this section we will discuss the alignment of charges or dipoles in condensed systems where one observes phase transitions following photoexcitation. To realize a coherent control of cooperative switching in ferroelectric materials has been an important challenge. This involved forcing the molecules of a material to transform and to strut in step under control. In order to understand such phenomena and to control them, ultrafast experimental tools have to be developed along with theoretical recipe to describe the evolution of the process both in time and space. Classic work in this area is on neutral (N) to ionic (I) phase transition in TTF-CA (tetrathiafulvalene-*p*-chloranil), a charge-transfer molecular material in which electronic and structural changes are strongly coupled [45].

An optical 300-femtosecond laser pulse switches the material from a neutral to an ionic state on a 500-picosecond time scale and cooperatively self-organizes into a long-range structural order. The phase transition and the molecular order is measured utilizing time resolved x-ray diffraction with a resolution of 100 ps (see Figure 6.14).
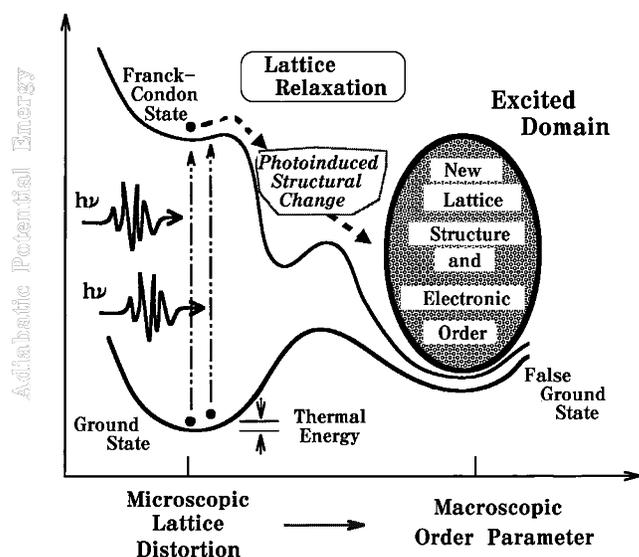


*Figure 6.13  Schematic drawing of the photoinduced transformation path along the polar order parameter P. The stable state is made of homogeneous, nonpolar neutral chains of molecules. Photons excite the ionic state and the coupling between the relaxed species makes the system switch to a transient macroscopic state with cooperative order. Courtesy:  Professor Keiichiro Nasu, KEK, Japan*

The development of intense sources of hard x-ray opens new opportunities for challenging experiments that require:

1) sub-picosecond time resolution, 100 fs or less, to probe the ultrafast coherent structural dynamics,

2) high flux to observe the transformation process from precursor clusters to long range 3D order as a function of control parameters, excitation density, temperature,

3) single-shot experiment to study the writing and the reading of information in a bistability regime, and

4) THz pump-x ray probe in the situation of polar precursor dynamics.

Future questions in this area would be about understanding the time evolution of local and nanoscopic order (domains) accompanying the transitions, characterizing time evolution of soft phonon modes around the phase transitions, time development of molecular displacements, etc. Hence the new challenge is to control the macroscopic photo-switching in materials which requires direct observation of ultrafast precursor phenomena that precede photoinduced phase transformation. The development of very intense femtosecond x-ray sources opens new opportunity to probe precursor phenomena which precede a photoinduced transformation.

The x-ray Bragg diffraction only probes the average periodic structure whereas the diffuse scattering latter fingerprints local deviations. Thus the time-resolved x-ray diffuse scattering can probe photo-generation of nano-domains. This is the most suitable method to bring out essential information about the mechanism of a photo-induced phase transition.
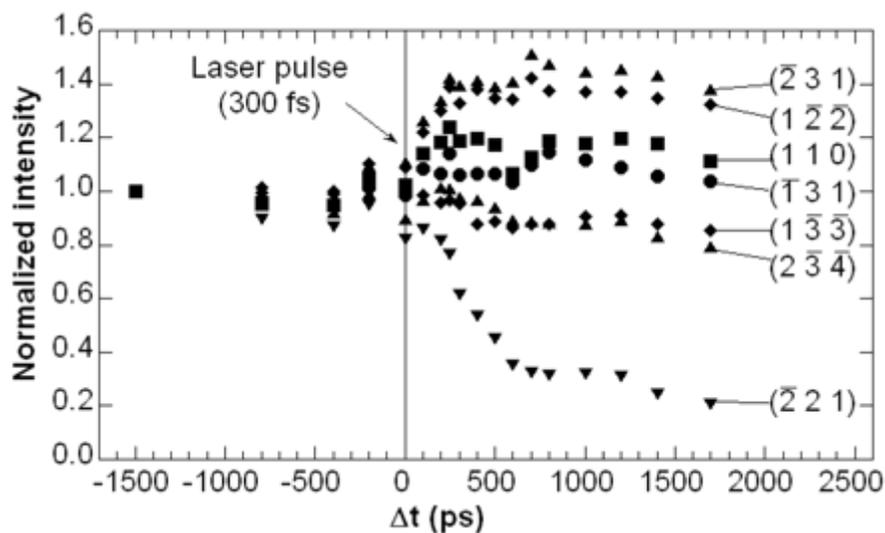


*Figure 6.14  Relative intensity of some Bragg reflections versus the delay between the laser pump and the x-ray probe. A large structural reorganization, associated with the neutral-to-ionic transformation, follows the laser irradiation. After about 500 ps, the light-driven metastable state is established [44].*
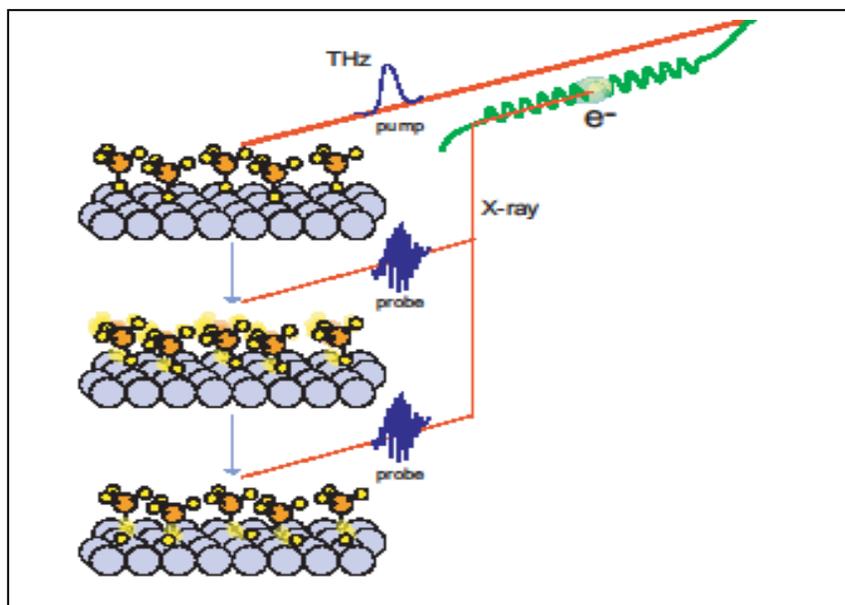
*Figure 6.15  Schematic sketch for the THz pump and x-ray probe experiment.
The molecular motion at surfaces to initiate the reaction is optically triggered
by the ultrashort coherent THz radiation. Time evolution of the reaction is
probed utilizing an ultrashort x-ray pulse [47].*

Thus, preliminary experiment [46] has shown the formation of 1D precursor cluster in a charge transfer (CT) crystal. However, the time resolution of 100 ps precluded to the observation of coherent nucleation dynamics, where femtosecond pulses should be required. Another fascinating question is how these precursor clusters can grow to establish the long range order. In CT molecular solids the formation of 1D nano-domains may induce coherent dimeric displacements.

Coherent control of these deterministic vibrational dynamics, for instance by sequencing and tailoring femtosecond laser pulses, is particularly exciting. New x-ray tools with picosecond to femtosecond resolution and nanoscopic to atomic resolution to perform diffraction, diffuse scattering, imaging, etc., along with plethora of complementary time domain techniques such as the Raman spectroscopy and ultrafast electron diffraction will enrich this area of complexity research.

The nature and yield of the products from the excitation of a broadband THz pump pulse can also result in coherent spatial manipulation of molecules. The probes for the resulting reaction leading to the product are the well-developed soft- and hard-x-ray tools with a pulse width of picoseconds to femtoseconds (see Figure 6.15) [47]. This approach complements the use of scanning-tunneling microscope (STM) tips to manipulate molecules on a surface utilizing a strong electric field
$(1-3 \times 10^9$ V/m) [48].

While THz excitation leads to collective manipulation, the STM will provide single-molecule manipulation on the surface. With an STM, new molecules can be constructed from the basic molecular building blocks on a one-molecule-at-a-time basis in a systematic step-by-step manner on the surfaces.

Owing to these advances, it has become possible for the basic chemical reaction steps - such as dissociation, diffusion, adsorption, re-adsorption, and bond-formation processes - to be investigated.

These capabilities will lead to new opportunities for combining the two pumps (STM and THz) and probe with a hard x-ray pulse – STM to build the chemical blocks on the surface and THz to organize them. Initial work on the surface structure of Cu(100) modified by chloride and iodide studied in an electrochemical environment by means of *in situ* STM in combination with *in situ* surface x-ray diffraction shows some very promising results [49]. The study demonstrates the ability to measure potential dependent surface relaxation phenomena. Performing such work in the time domain would be a productive in future [50].

## 6.5  Nano-scale Machines

The natural advance from the concept of manipulation of single molecules is to build nano-motors and *nano cars,* These single-molecule-sized nanoscale machines with controlled mechanical motion travel in liquids or on surfaces in response to external stimuli such electric fields or photoexcitation [51]. In Figure 6.16, a set of fabricated nanocars are shown [52].
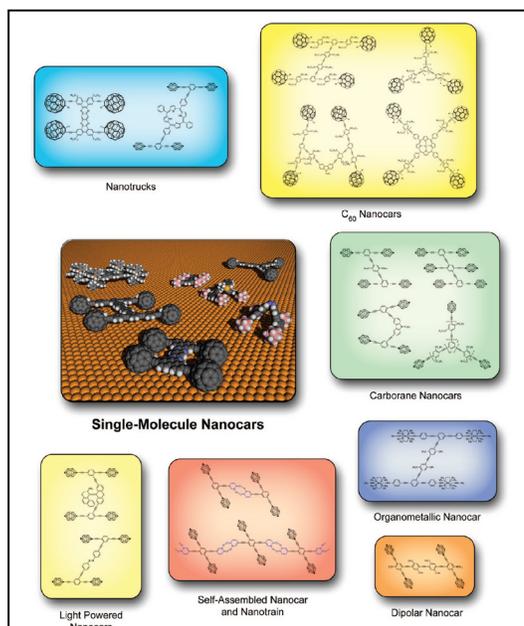


*Figure 6.16  Overview of single molecule nanocars that have been synthesized [52].*

The main challenge is understanding the new rules of behavior, because the non-equilibrium interaction of molecules on surfaces and nanoscale systems lies at the threshold between classical and quantum behavior that do not exist on the larger scale. Their response to external stimuli and motion in liquids and on solid surfaces begs more questions than answers. At the same time, these achievements open the way to entirely new opportunities in surface catalysis, nanochemistry, and nanochemical technology. For example, adsorbate motions are the most fundamental steps in surface chemistry [53] and are typically the rate-determining steps. The challenge is to observe molecular motions and energy redistributions with a time and spatial resolution sufficient to capture the key details. Studying the movement of adsorbates induced by electric fields, phonons, photons, or electrons is therefore of paramount interest. In the new era of control science, one explores different approaches to guide the reaction process involving a single reactive encounter such as absorbate motion or an assembly of molecules forming a nano vehicle. The future x-ray light sources will have opportunity to probe unique aspects of nano-systems. For example, combining hard x-ray tools and laser tools with the STM-controlled single-molecule/reaction study will supplement an unexplored dimension of chemical, structural, and temporal identification. The combination of THz and x-ray spectroscopies could provide a unique opportunity for XFELs to conduct ultrafast chemical studies of single-molecule reaction paths on surfaces. With enough effort, there are possibilities to visualize the workings of nano motors/nano cars in full detail in real-time x-ray movies [54].

Investigations of molecular manipulation on the surfaces and studying the temporal development of chemical order is a fertile area for future studies utilizing spatiotemporal hard x-ray tools covering time domains from milliseconds to femtoseconds [55]. These achievements open entirely new opportunities in catalysis, nanochemistry, and nanochemical technology.

## 6.6  Future Outlook

The evolution of complexity in chemical systems can best be described as a response to external stimuli, such as photoexcitation, in the time domain which can be quantified by measuring the changes in electronic structure of chemical bonds, their lengths and angles. Chemical reactions and physical transformations discussed by this panel involve the breaking and rearranging of intra- or intermolecular bonds for which the time scale of fundamental steps is on the order of femtoseconds to picoseconds and distances in the in angstroms scale. How do all these things behave in a correlated way, 'dynamically' in time and space, both at the electron and atomic levels? Ample examples were discussed in this chapter that have given an early glimpse of both the evolution and control of complex chemical process in gas, liquid and solid phases of matter. In particular, we addressed the structure of the transition state, quantum control of chemical reactions, dynamic propagation of the reactions, and their relevance to energy conversion, information storage and nanomotions. The field of control science of complexity is in its infancy, and future demands instruments that can be applied to every area of chemical dynamics with the power to resolve molecular bond lengths spatially and molecular vibrations temporally. Such extraordinary instrument would be an x-ray free-electron laser, preferably a seeded source with high pulse rate, to follow the evolution of molecular motion in real time. Nonlinear and multidimensional spectroscopy studies utilizing such a source would produce controllable x-ray- or light-

fields that perturb a molecule and subsequent x-ray-fields see changes in the molecular states. For this kind of spectroscopy, it is important that the different pulses interact with the molecular states over very short time periods, in such a way that the tailored information imparted by the first light pulse doesn't get lost or dissipated. Hence the control studies of the evolution of complexity will require fully coherent, ultrashort (~ femtosecond), energy-tunable x-rays with controllable polarization fields and pulse-shaping capabilities. The control of source parameters, such as the harmonic powers, high brightness harmonics, and high repetition rate, need to be defined for each investigation. Initial studies will focus on chemical evolution in simple systems such as gas phase molecules, advancing to more complex systems involving the study of photochemically induced bond breakage in solutions and the subsequent recombination within the solvent cage. Photosynthetic processes present a higher level of complexity that will be the final bastion of grand challenge. Although the panel focused on hard x-rays, a similar FEL source of soft x-rays would fulfill the need for tunability at the C, N, and O K edges.

The progress in control science in addition requires improved theory to predict the electronic structure for novel electronic configurations in both simple molecules and much larger complex systems. Such improvements will be essential for a large range of studies, first from an experimental view to maximize and control particular reactions through the excitation of specific resonances or polarization states; but most importantly to establish the evolution and control of complexity in chemical systems as a true science.

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# 7 Focus Panel: Controlling Biological Functions

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| *Chairs:* | *Sol Gruner* | *Cornell University, Ithaca* |
| | *Ian McNulty* | *Argonne National Laboratory* |
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| | *Hettel, Robert* | *SLAC National Accelerator Laboratory* |
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| | *McIntosh, Andy* | *University of Leeds* |
| | *McNulty, Ian Laurence* | *Argonne National Laboratory* |
| | *Moffat, Keith* | *The University of Chicago* |
| | *Ourmazd, Abbas* | *University of Wisconsin, Milwaukee* |
| | *Rosenbaum, Gerold* | *University of Georgia and Argonne National Laboratory* |
| | *Schlichting, Ilme* | *Max Planck Institute for Medical Research* |
| | *Schmidt, Marius* | *University of Wisconsin, Milwaukee* |
| | *Schwander, Peter* | *University of Wisconsin, Milwaukee* |
| | *Spence, John Charles* | *Arizona State University* |
| | *Wakatsuki, Soichi* | *Photon Factory, KEK, Japan* |
| | *Weckert, Edgar Franz* | *Deutsches Elektronen Synchrotron* |

## 7.1  Introduction

Biomolecular machines of living cells are made from soft materials: biopolymers like proteins and RNA. As opposed to macroscopic machines, biomolecular machines experience thermal motions that play an important role in biological function defined as a manifestation of living activity. These biological functions create energy movement through chemical reactions necessary to perform many types of life-sustaining work that facilitate communication and other necessary interactions between the components of a living organism and its external environment, all of which belong to the field of non-equilibrium science. The ultimate goal is to control the quantum details of chemical reactions with particular emphasis on electron transfer, and to identify global motions that may be necessary for long-range control of chemical reactions. The functional behavior extends at all levels of description of biological systems, from proteins to cellular to the multicellular scale and all the way up to the level of organs, organisms, and populations of organisms. Most biological functions consume and dissipate energy and are far from equilibrium [1]. The dynamics involved in these functions results from nonlinear interactions that link molecular mechanisms with the surroundings.

The biofunctions occur over different time and length scales. For example, in the processes involving biochemical electron transfer, such as catalysis, molecular recognition, signal transduction, chemical sensing, or allosteric reactions, fluctuations occur on the femtosecond to picosecond time scale (femtosecond biology is not a myth!) and sub-angstrom structural scale. On the other hand, at a cellular and multicellular level, large-scale motions involving fluctuations of several angstroms and time-scales of nanoseconds to seconds will control protein folding; this also includes physiological functions and biomechanics of small organisms. The energy involved in many of these processes is comparable to thermal energies (see Fig. 7.1) [2]. The physiology and biomechanics of small organisms, or the growth of biological cells and tissues, spread over large time and spatial domains, typically from a few hundred microns to nanometers, and the temporal scales of their dynamics will change from milliseconds to sub-picoseconds. Some of the more common processes include copying of DNA (replication), creation of messenger RNA from genes (transcription), and RNA conversion to proteins by ribosomes (translation).

There has been very heavy emphasis on protein structure determination utilizing hard x-ray sources during the past 3 decades. Thus the field of structural biology is an extremely successful field of the life sciences with over 60,000 structure entries in the Protein Data Bank. This mass of structural knowledge has provided detailed biological insight into protein structure and function relationships and uncountable details into the specific biochemistry of cellular reactions [3].

In the next few years with the availability of free-electron x-ray sources, ultrashort x-ray pulses of high enough intensity and of sufficiently short duration (20-50 fs) to obtain single-shot diffraction patterns from a sample before significant damage occurs. This diffraction before destruction method may enable the determination of structures of proteins that cannot be grown into large enough crystals or are too radiation sensitive for high-resolution crystallography. It will be possible utilizing x-ray FEL sources to record millions of diffraction patterns that can be used to assemble 3D patterns for structure determination, perhaps from a single molecule [4].
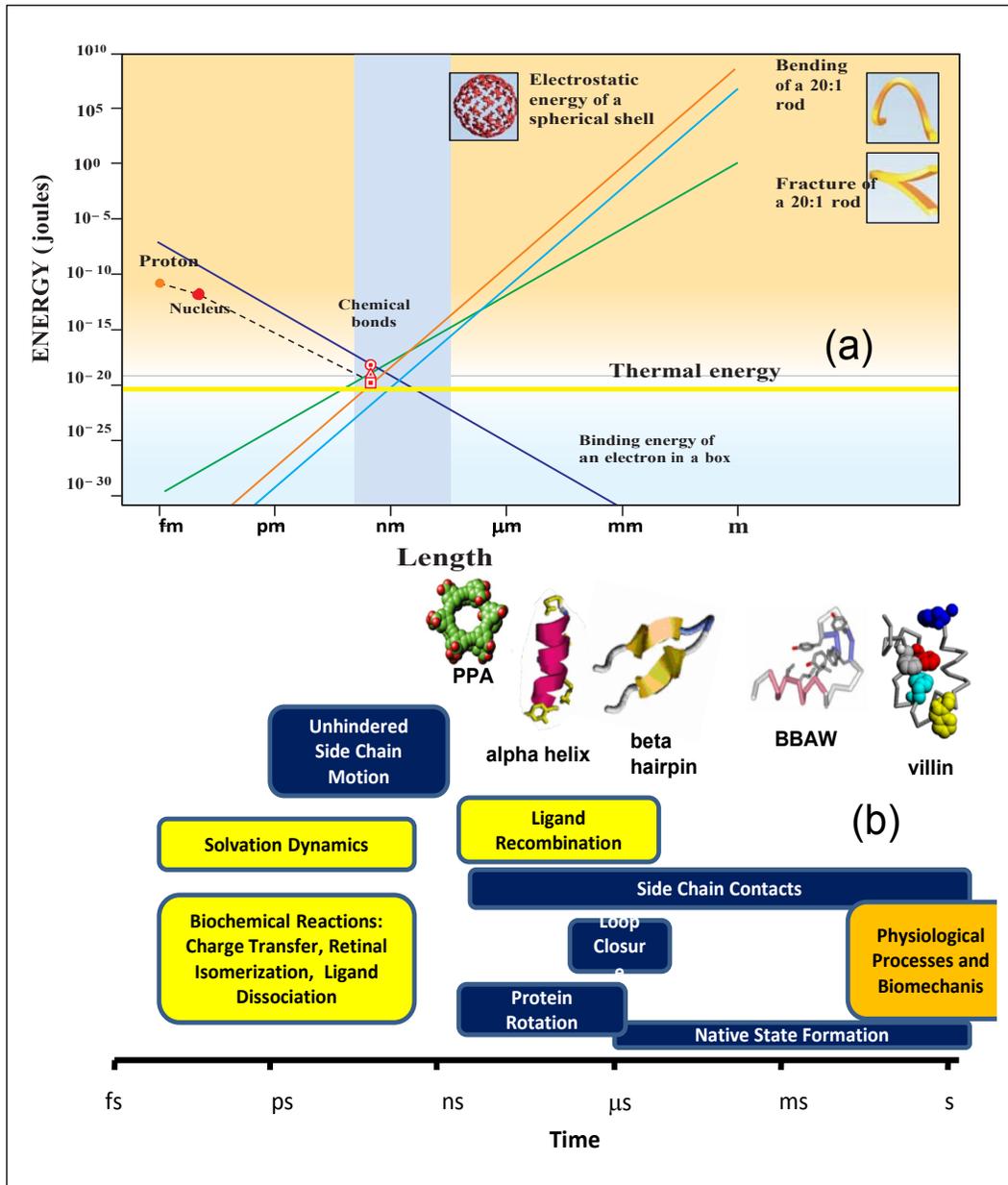
Figure 7.1 (a) Correlation between object size and the thermal, chemical, mechanical and electrostatic energies involved. The red square, triangle and circle correspond to the energies for hydrogen bond, phosphate group of ATP and covalent bonds (from reference 2). (b) Time scales of various biofunctions discussed under biochemical reactions, protein folding, and physiological and biomechanical processes. The molecular structures depict protein folding sequence in time.

Despite this impressive history and future potential for success, understanding the details of protein conformational changes presents a much bigger challenge for structural biology. Indeed the non-equilibrium biochemical/biophysical processes intrinsic to biomolecular functions have received attention from the x-ray community during the past decades. Most popular x-ray methods use the intense x-ray beam from third-generation synchrotron sources to study the time evolution of complex bimolecular processes. They include (a) time-resolved Laue diffraction to measure three-dimensional structural changes in proteins in real time, (b) monochromatic x-ray diffraction from intermediates trapped at low temperature, (c) time-resolved wide-angle, small-angle, and diffuse x-ray scattering are emerging methods applicable to proteins in non-crystalline environments such as liquids, and (d) time-resolved x-ray absorption spectroscopy studies of proteins. These x-ray techniques have aided in time-resolved probing of systems that have been excited utilizing an external energy source such as a light pulse from an optical laser [5]. With the availability of highly intense x-ray free-electron lasers (XFELs) that produce 10-100 fs x-ray probe pulses one expects new advances in methods to interrogate the evolution of a biophysical or biochemical sub-picosecond processes in their early stages. Time-resolved x-ray structure analysis utilizing femtosecond crystallography is especially interesting for the membrane protein complexes involved in photosynthesis, and opens new avenues to unravel the molecular mechanism of water splitting in Photosystem II [6]. Present understanding of protein functions such as ligand binding and signal transduction and of protein and peptide folding mechanisms has been aided significantly by the use of structure-sensitive time-resolved optical spectroscopies [7]. Variety of time-resolved x-ray spectroscopy and scattering techniques at the storage ring x-ray sources with under 100 ps resolution and modern detectors will allow one to probe the dynamics in the nanosecond to sec range [5].

In addition to the use of optical triggers to initiate a reaction, T-jump [8] and rapid mixing of two fluids at the tip of the liquid jet allow one to record snapshot diffraction patterns at different points along the liquid stream as the ultrafast reaction proceeds [9]. A method for determining a comprehensive chemical kinetic mechanism in macromolecular reactions has been developed through a method based on five-dimensional crystallography, where, in addition to space and time, temperature is also taken into consideration [10]. This has allowed the extraction of relaxation times of the reaction at the two temperatures. A newer approach of combining low-resolution SAXS data obtained from solution scattering has been combined with computational methods to reconstruct low-resolution structural models of large multidomain complexes and multidomain proteins [11]. The scattering data can serve as independent constraints for computational modeling to ultimately characterize the structures/shapes of large protein complexes. The approach has the potential to be used in the time domain to investigate an evolving biomolecular structure in solution.

## 7.2  Light-triggered Studies of Photosensitive Biomolecules

Many organisms have developed the ability to interact with light, because light serves as a near-ubiquitous source of energy and information. Light can be utilized either for its energy content, e.g., in photosynthesis, or for its information content, e.g. in phototactic responses in which an organism or a cell moves toward or away from a source of light. Light-sensing component of these organisms is a

protein, i.e., biological photoreceptors containing a light-absorbing chromophore. The various photoreceptor proteins that have been described in the literature can be classified into a limited number of families. These families are the rhodopsins (containing retinal), the phytochromes (binding a bilin derivative), the xanthopsins (containing a covalently bound 4-hydroxycinnamic acid), and the cryptochromes, the phototropins and the BLUF proteins that all contain a flavin derivative. Activation of these photoreceptor proteins involves changes in the configuration of the corresponding embedded chromophores. For the first three families, this change in configuration is a trans/cis isomerization, but for the flavin-containing photoreceptors other types of photochemistry involving light-oxygen-voltage (LOV) sensors have been uncovered. This change in configuration of the chromophore then initiates formation of a signaling state of sufficient stability in the surrounding apo-protein to propagate the knowledge of photon absorption to a downstream signal transduction partner [12].

Chlorophyll *a* is the main photosynthetic chromophore in all organisms (except bacteria), and is supported by other photosynthetic pigments such as chlorophyll *b* and located in the membranes of the thylakoids. The photoabsorption occurs in the thylakoid membrane. The dissociation of electrons leads to the formation of ATP and NADPH, which are needed to produce glucose. Hence the femtosecond transfer of electronic charge upon photoexcitation plays a fundamental role in the function of many organic and biomolecular systems, such as individual organic chromophores. Some of the literature cited earlier [5,6] illustrates the use of x-rays tools directly to observe structural changes with atomic resolution on the timescale of the strongly damped collective modes and in turn investigate the structure-function relationships. The relevant time resolution required is nominally sub-picosecond for 10 -100 cm-1 modes as inferred from vibrational energy relaxation and collisional transfer to the water layer.

There are four families of photoreceptors that contain Flavins as the chromophore. These photoreceptors detect blue light, for example, in plants, bacteria and other microorganisms [13]. The photocycle in each of the photoreceptor begins with the absorption of blue light by the flavin molecule to excite one of the vibrational levels such as S1, S2…These states will de-excite through process such as fluorescence, internal conversion, intersystem crossing, and phosphorescence. The de-excitation of S1 state in flavins is known to use intersystem crossing pathways due to spin-orbit coupling to occupy isoenergetic vibrational levels such as T1, T2, etc (see Fig. 7.2) [14]. Although the photocycle in these receptors have been studied in detail during the past decade [13], they have not yet been investigated utilizing any of the ultrafast x-ray tools. There is a propensity of examples similar to this involving natural and artificial photosynthesis all of which will be suited for ultrafast x-ray studies. The spatiotemporal time resolution of x-ray tools will enable a direct determination of the atom-atom correlation functions to cast out the key modes coupled to the reaction coordinate.

This has been demonstrated in the past studies of simple molecules [5,6,9] that have addressed some of the following important questions:

- *How can we observe an evolution of light-initiated biochemical reactions utilizing time-resolved x-ray scattering (WAXS and SAXS) and spectroscopic methods?*

- *How could we benefit from time-domain x-ray spectroscopy in elucidating ET process in the photoexcited biological complexes?*
- *How does the solvent shell reorganize in time after the photoexcitation of the molecule?*
- *Can we extend the success of time-resolved optical polarization spectroscopies to the x-ray range?*

In future there will be opportunities to answer the same question in the study of optogenetic reactions discussed in the next section.
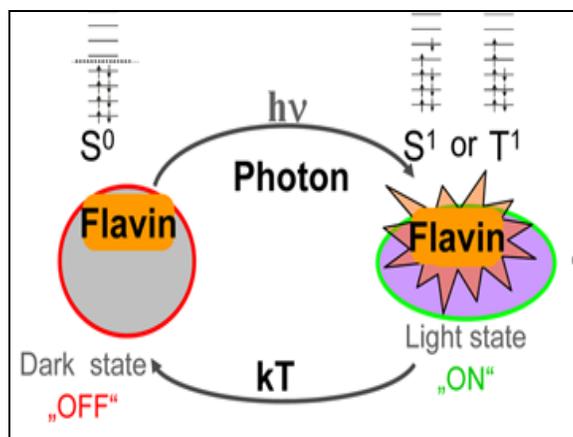


*Figure 7.2  Photocycle in a typical flavin containing blue-light receptors [Courtesy: I. Schlichting, 14]*

### 7.2.1  Optogenetics

Although the function of most proteins and biomolecules is not inherently light-dependent, in many cases it can be made so, e.g. through modification with a photosensitive chemical moiety or with engineered photoreceptors that are genetically caged compounds, in which the cage is provided by a photosensor domain [12]. The two approaches have some differences, but their application in future opens new doors to the field of optogenetics (see Box 1).

The light sensitivity of natural and engineered photoreceptors is provided by one or more photosensor domains that use protein targets. The key advantage of engineered photoreceptors is their ability to be genetically encoded; they can be introduced to the target organism, tissue or cell as DNA templates. Photoreceptors detect light through absorption of photons by their chromophore cofactor. Photocycle begins following light absorption that typically comprises of changes in the conformation, dynamics and function of the chromophore and the surrounding protein moiety. The photocycles are usually reversible and the photoreceptor thermally reverts to its ground state. The photocycle is accompanied by distinct electronic changes that have been studied by UV and optical spectroscopies. Since photosensor domains can readily be coupled to effector domains through a linker molecule, in future one can control the light-induced changes in biological activity. Signal is generated by absorption of a photon in the sensor domain, and transmitted via the linker to the output domain Photo-excited structural changes often involve N-and C-terminal α-helices of the effector and sensor domains.

Structure-specific interaction between the input and output domains is not always evident and understanding the role of linker will also be of great importance.

As an example [15], histidine kinase is generally a light-inert enzyme but its activity can be initiated by oxygen molecules that catalyzes the chemical reaction

ATP + protein L-histidine $\Longleftrightarrow$ ADP + protein N-phospho-L-histidine.

Can we design, engineer and test a blue-light-sensitive histidine kinase? In other words can the reactions initiated by oxygen molecule in this enzyme be replaced by sensitivity to blue light? A potential design of a blue light sensitive histidine kinase is shown in Fig. 7.3.

The knowledge gained so far from the use of x-ray spectroscopy and scattering studies on light-sensitive molecules [5,6] could be applicable to optogenetic systems.

However there are many challenges even if we believe that any biological activity can be made light sensitive through an optogenetic approach. We present some them here:

- *How fast does the optical signal generate information in the receptor molecule?*
- *How fast is this information signal transmitted to output domain through the linkers?*
- *How fast does the effector molecule respond and modulate the biological activity?*
- *Electron transfer and isomerization are probably the only chemical photoprocesses that are fast enough for 100 ps and femtosecond studies utilizing the x-ray tools available to us today and in the near future. Indeed these will allow us to investigate what we will call 'femtosecond biology.'*
- *While optogenetic functions can be demonstrated in molecules, can such light harvesting functions perform in crystalline state to be suitable for x-ray investigations?*
- *Are the optogentic processes repeatable so as to allow excellent S/N measurements of x-ray movies with femto-resolution of electronic and structural maps?*
- *Can we address these questions in the next decade and develop general principles to confer sensitivity to light on otherwise light-insensitive systems, such as transcription factors or enzymes such as histidine kinases? The answer is yes.*

The development of powerful new x-ray tools with femtosecond to 100 ps to ms resolution will extend their applications to cell biology and biophysics and to the reach of optogenetics, namely engineered photoreceptors, to make major contributions to the neurosciences.
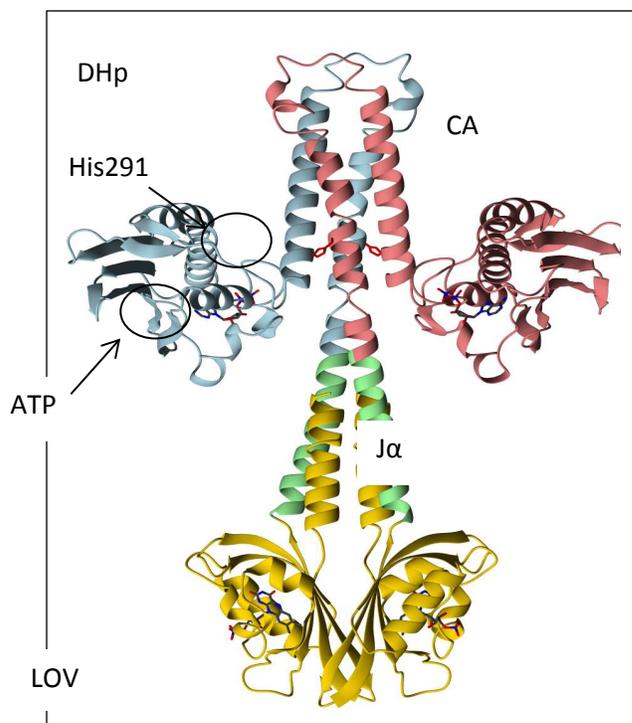
*Figure 7.3 Design and signaling mechanism of blue-light-regulated histidine kinases. The sensor (LOV) and effector (DHp) domains are connected by amphipathic a helices (Jα) and are linearly arranged around the dyad symmetry axis. Jα helix linker could form continuous helix with DHp domain. Signal detection in the LOV (light-oxygen-voltage sensor) domain could generate torques around the dyad axis which can be integrated and propagated to the histidine kinase domains (Courtesy: Keith Moffat).*

### 7.2.2  Coherent Control of Biological Functions

Much of the biology takes place in the liquid state with the solvent playing a critical role in determining the overall thermodynamics and kinetics of various processes, including those associated with enzymology, or protein folding and molecular architecture, or cell division, or muscle contraction, or cell motility, or animal locomotion. As has been discussed above, the light pulses have been generally used to initiate various biological processes that alter the molecular geometry due to electron transfer between the charge donating and accepting groups as well as from polar salvation. During the past few years pump-probe x-ray spectroscopy and x-ray scattering tools have addressed these questions on structural dynamics of solvated molecules and solvation shells as they go through the non-equilibrium pathways following photoabsorption [16]. Can we manipulate these biological reaction pathways that span a very wide length (0.1 nm to 1 m, 10 decades) and time (femtosecond to kiloseconds, 18 decades) scales by controlling the excitation light waves? Can only one of these reaction pathways proceed with a control over the increase or decrease in its quantum yield, while blocking the other paths through coherent control?

Most biological reactions and important physical processes occur in the condensed phase, where interactions of the system with the fluctuating bath may lead to the destruction of the coherence in matter involved in the reaction. In fact, the processes (outlined in Sections 7.2 and 7.2.1) are usually considered to be driven by incoherent phenomena hence fail to realize coherent control. At the same time, proteins are highly evolved structures, and the question arises whether the phases of the underlying matter waves could play a role or even be manipulated in directing biological processes. Coherent manipulation of the phase and amplitude of excitation light waves can capture the underlying molecular dynamics driving the selected process. Thus the coherent control experiments explicitly exploit the wave nature of matter which can create interference pathways to enhance or suppress an observable of interest [17].

Photoisomerization of the retinal chromophore is a perfect example to illustrate quantum control in complex biological systems. This system has been investigated with TR- SAXS [18] that has shown the structural changes associated with the charge transfer following photoabsorption, retinal isomerization, and finally the ligand dissociation (Fig.7. 4). These observations are consistent with the molecular description of the ultrafast trans-cis isomerization process from the all-trans to a 13-cis configuration along with additional changes in the conformation of Bacteriorhodopsin (bR) (see Fig. 7.4).

This system lends itself experimentally to test the above discussed ideas on coherent control and more specifically address whether the quantum coherence persists long enough to influence a biological function [19]. One of the most important observations made utilizing optical spectroscopy in this work was the linear intensity dependence of the photoisomerization yield on the amplitude of the excitation laser pulses.

The achieved control of the isomerization yield was 52% and 78% for the anti-optimal and optimal pulses, respectively. This experiment was the first to demonstrate both constructive and destructive interference effects in controlling a biological function. A number of models have been developed and compared with more recent experimental results [20]. However many questions still remain to be tested which will require temporal probing of atomic motion, both locally and globally, during the photoisomerization process (Fig. 7.5). This might provide needed information on the coherent evolution of the responsible vibrational wave-packets on the excited-state potential energy surface in complex biological systems.

In the coming years we expect TR-SAXS movie to be measured depicting the atomic motion when the system is subjected to coherently controlled amplitude of the laser wave field. Such measurements will provide further insight on the selective paths of photoreaction that are coherently controlled [17].There are many phenomena such as photosynthesis that are similar and of practical importance in artificial energy harvesting. In future we expect a general application of quantum coherent control methods to study chemical and biological processes along with the probing of atomic motions involved utilizing ultrafast x-ray techniques.
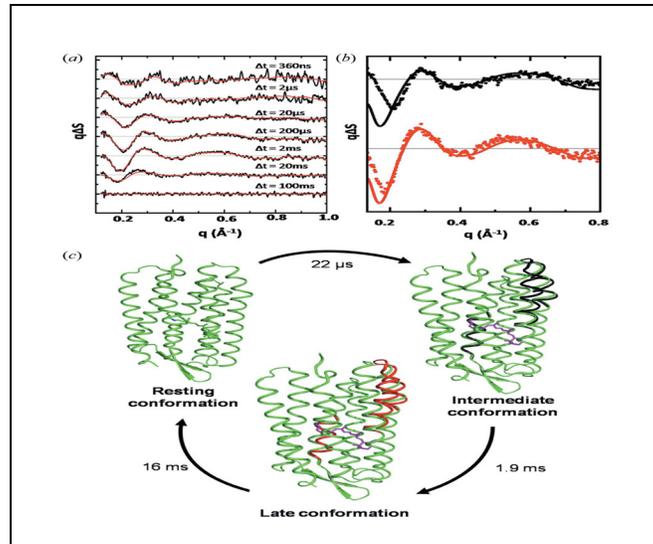
*Figure 7.4 TR-WAXS data from solubilized samples of bacteriorhodopsin. (a) Integration in rings and subtraction of `laser off' images from `laser on' images yields the difference scattering curves as a function of the time delay (Δt) between photoactivation and the x-ray probe. (b) Basis spectra of an intermediate and late conformational state extracted from spectral decomposition of the data shown in (a). (c) Structural interpretation of these data utilizing a rigid-body minimization routine illustrated in terms of the bacteriorhodopsin photocycle (doi: 10.1016/j.str.2009.07.007) [18]*

## 7.3 Protein Folding

In understand protein folding we should ask: How does a protein adopt the correct structure? What drives the folding process? What controls the folding in living cells? How does a protein search and converge quickly to native states in less than a microsecond? The protein dynamics along the folding pathway is governed by a complex multidimensional energy landscape. Folding advances by a trade-off between energy and entropy as the protein moves down the landscape, but both energy and entropy eventually descrease.

## Box 1
## Light Engineering: Optogenetics

*Can one control nerve cells with the aid of light: this is made possible by optogenetics which use light-responsive proteins ("opto-") encoded in DNA ("-genetic"). Optogenetic devices can be introduced into tissues or whole organisms by genetic manipulation and be expressed in anatomically or functionally defined groups of cells. It enables, for example, the investigation of neurobiological processes with unprecedented spatial and temporal precision. The key tool of optogenetics is the light-activated protein.*

Gero Miesenböck
The Optogenetic Catechism
Science 326, 395-399 (2009)
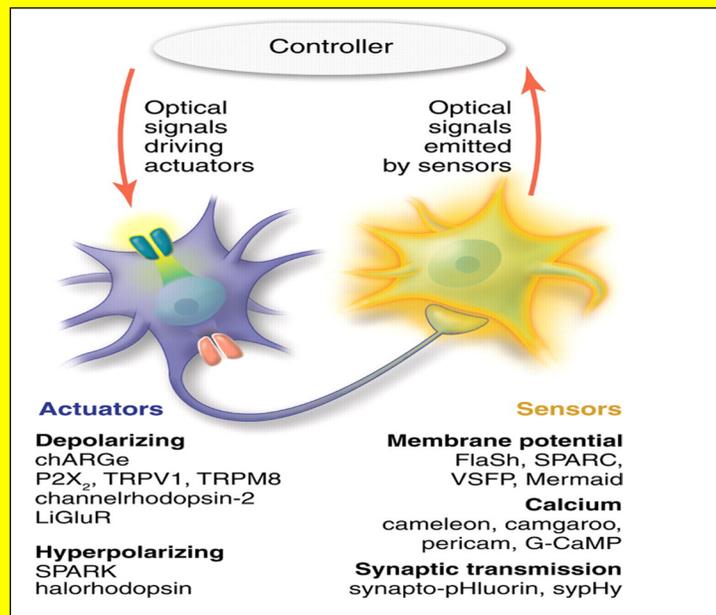


*Light-driven actuator proteins are utilized to control genetically targeted cells in a circuit. The actuators transduce optical commands into de- or hyperpolarizing currents. Light-emitting sensor proteins report changes in membrane potential, intracellular calcium concentration, or synaptic transmission. Can we probe the structural evolution using x-ray tools along the path of neurobiological processes?*
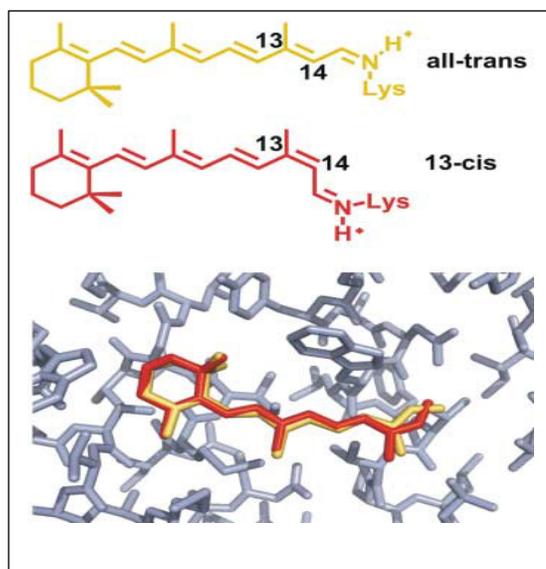
*Figure 7.5 Configurations of the retinal molecule (top) in bacteriorhodopsin (bottom) in the ground state (all-trans, yellow), and after isomerization (13-cis K form, red). The bottom image is from the Protein Data Bank; identification numbers 1QHJ and 1QKP. The photoisomerization process requires a torsional motion and bond stretching along the C13- C14 axis (from Ref. 19).*

The shape of landscape is governed by many local and environmental factors. For example, in addition to the amino acid sequence of the protein, it would be governed by solution properties such as pH, temperature, solvation behavior, interaction with neighboring proteins, etc. It is hard to comprehend how quickly (< microsecond) the protein chooses a specific path to achieve the right conformation out of gazillions of available conformational states in the energy landscape (so called 'Levinthal paradox' [21]). It is now accepted that the protein is funneled down the free-energy landscape by energy barriers, kinetic traps and narrow pathways [22-24]. The cross-sectional view of the energy funnels in Fig. 4 shows various tiers of energy as well as various unfolded states at the edges of the funnel which ultimately converges to the minimal energy state.

A folding funnel represents an ensemble of unfolded nascent polypeptide chains flowing through many microscopic conformations that may be grouped to form macroscopic pathways leading eventually to native ground state. Dynamics on a 'slow' timescale of many microscecond to milliseconds (tier-0 dynamics in Fig. 7.6) define collective fluctuations between macroscopically distinct states that are separated by energy barriers of several kT. This dynamics has been observed for example by TR-SAXS [25]. 'Fast' timescale dynamics (tier-1 and tier-2 dynamics) represent small groups of atoms fluctuating collectively on the nanosecond timescale (such as loop motions) and local atomic fluctuations on the sub-picosecond timescale (such as side chain rotations). This dynamics of microscopic conformations is separated by energy barriers of less than 1 kT at physiological temperature. The time-domain WAXS

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measurements mentioned earlier are useful in this femtosecond-picosecond timescale to investigate this dynamics [5,6,9].

Utilizing a combination of computational, theoretical, and experimental approaches such as those in Fig. 4 and time-domain SAXS or diffuse scattering, the folding dynamics of protein complexes can be explored toward understanding both the physical principles governing protein behavior and the role of protein folding in cellular functions (see Fig. 5). A major challenge is to perform molecular dynamics (MD) computational simulations over femtosecond to millisecond timescales.

In MD simulations the presence of fast vibrational motion constrains the fundamental integration time-step to femtoseconds. It allows for representations of solvated proteins to tens of nanoseconds or even to several microseconds (Fig. 7.7). However, such simulations are currently limited in several respects: the ability of molecular dynamics force fields to reproduce the true potential energy surfaces of proteins in their true environment, the need of simulations to extend to the time scale of millisecond folding, and the difficulty of sampling and analysis to capture the extremely heterogeneous folding processes. Pump-probe protein-folding experiments also require very careful assessment of non-equilibrium energetics such as denaturation from physical and chemical stress. Protein folding involves numerous cooperative non-covalent interactions whose individual magnitudes can be less than a kilojoule per mole, leading to a complex, locally random-looking free-energy landscape discussed above. The pumps that are generally used to initiate non-equilibrium unfolding or folding processes are pico- to nanosecond laser-induced T-jumps, pH-jumps, mixers, etc. The energies from these pulses are comparable to energetic protein dynamics, which is contributed to many effects such as hydrophobic, hydrogen bonding, salt bridge, surface solvation, solvent structure, and other effects.

Additionally these studies are best performed in standardized native solution conditions. For the next-generation spatiotemporal x-ray studies, there is a need to develop such micro- or nano-diffusional-mixers where the sample is hydrodynamically focused to submicron dimensions and sampled at a fast rate. However the energy of an x-ray photon, 50-70 Kcal/mole, far exceeds that required to completely unfold a protein. How to usefully harness this energy and minimize damaging side-reactions? Thus far, much of the knowledge that has been experimentally gained on protein folding is from optical and NMR spectroscopies. Developments in data analysis and time resolution in TR-SAXS will allow medium-resolution structural refinements of intermediate structures along reaction pathways. For example, the initial stages of the folding of b-lactoglobulin (BLG), a 162 amino acid, b-barrel protein found in bovine milk has been measured utilizing TR-SAXS [24]. The collapse from an expanded to a compact set of folded states was directly observed on the millisecond time scale from these measurements, and rarely one expects the folding times to be below10-20 $\mu$s. Hence these are ideal studies that one can perform utilizing x-ray pulses from storage-ring sources or even with the use of fast x-ray detectors. The coherence and high peak flux of the future XFEL sources would specially focus in tier 2-3 (Fig.4) to obtain temporal paths in the femtosecond-nanosecond time range utilizing a host of x-ray tools
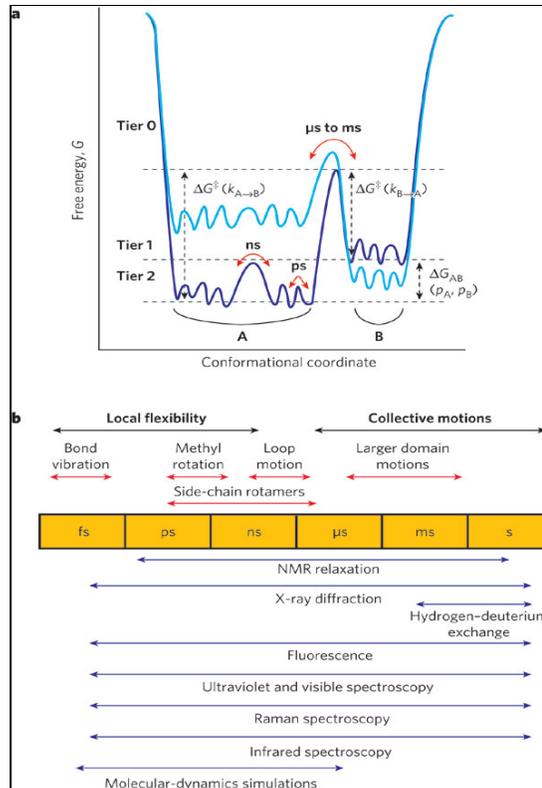
*Figure 7.6  The hierarchy of energy barriers in protein dynamics [24]: Tier 0, with ΔG > kBT, dictates large conformational change on the μs and slower time scale. Tiers 1 and 2 represent finer motions of loops and side-chains. There are finer femtosecond fluctuations involving bond vibration and the motion of solvent molecules. The techniques cover various temporal regions.*
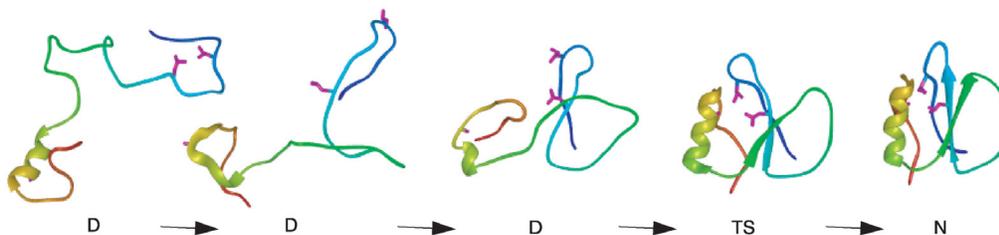


*Figure 7.7  Folding pathway of CI2: The MD unfolding simulations from the native state N to the denatured state(s) D are at 225C. The times are those of unfolding, and the structures are colored from red at the N terminus to blue at the C terminus. The 3-, 2-, and 1-ns structural snapshots, shown from left to right, are members of the D ensemble. The transition state, TS, is formed in 225 ps (http://dx.doi.org/10.1016/S0092-8674(02)00620-7) [26].*

The ultimate hope is to develop a full description of the energy landscape and its rugged nature among different conformations. In the next section, a new approach to biological dynamics that uses ultrashort coherent x-ray pulses from XFELs is presented.

## 7.4 Correlated X-ray Scattering (CXS) to Track Enzyme Catalysis

The role of conformational changes in explaining the huge catalytic power of enzymes is currently one of the most challenging questions in biology. Enzyme-driven catalysis controls most metabolic pathways in all living organisms, yet is poorly understood. A new method to track the conformational changes during enzymatic catalysis has been proposed [27] that uses the high flux contained in an ultrashort (tens of fs) x-ray pulse from an XFEL. The technique measures correlated x-ray scattering (CXS) from droplets of solution of biomolecules in non-crystalline form in which enzyme molecules can go through their catalytic cycles under close to physiological conditions. The CXS measurement requires that two photons from a single x-ray pulse are scattered from the same molecules contained in a droplet and is independent of molecular orientation. The time resolution of the scattering is obtained by pre-mixing enzyme and substrate at prescribed time delays relative to the droplet being exposed to the x-ray beam. The occurrence of the CXS events is greatly amplified by the number of macromolecules in the droplet and the high flux in the x-ray pulse.

The major challenge in these measurements is the requirement to control the formation and transport of the droplets containing the molecules to the XFEL x-ray beam, and this has been successfully developed [28]. Since exposure to the x-ray pulse happens for times on the order of 10's of fs, the molecules in the droplet do not have time to undergo significant Brownian motion during the exposure. Thus, two-photon scattering from any molecule in the ensemble happens for a given molecular orientation and internal conformation.

In an actual experiment, correlated scattering events are recorded at different pixels in an area detector defined by a pair of scattering vectors, q and q'. The two-photon CXS events are described by a four-point correlation function $C4(q,q',\cos\theta)$ :

$$C4(q,q',\cos\theta) = \left\langle I(\vec{q})I(\vec{q}') \right\rangle - \left\langle I(\vec{q}) \right\rangle\left\langle I(\vec{q}') \right\rangle \tag{1},$$

where $I(\vec{q})$ and $I(\vec{q}')$ measures the number of photons in the pixel defining a scattering vector $\vec{q}$ and $\vec{q}$, respectively, and the correlated average $\left\langle \ \right\rangle$ in the first term is taken over all pairs of pixels subtending a fixed relative angle θ. $\left\langle I(\vec{q}) \right\rangle$ and $\left\langle I(\vec{q}') \right\rangle$ are the usual two-point SAXS scattering average over all orientations. An advantage of CXS relative to the usual single photon SAXS measurement is that the background subtraction is self-generated by the act of correlating the data, with subtraction of the product of average scattering in the two-wave vector channels |q| and |q'| represented in the above equation. In a 1-μm-sized droplet there are typically $10^8$ molecules of protein solution at a concentration of 10 mg/ml [28]. A single x-ray pulse from an XFEL beam focused to an area of ~1 μm$^2$ will generate an estimated $10^7$ two-photon CXS events from such a drop. The measured CXS profile will fingerprint for a possible intermediate conformation expected to be occupied in the catalytic cycle. Thus, a full

experiment will involve such measurements performed as the catalytic cycle evolves over time. One measures such correlations from various droplets, each of them representing a differing catalytic cycle determined by the mixing of enzyme and substrate. CXS presents a revolutionary new method with which to directly observe the conformational changes essential to understanding the catalytic function.

In order to illustrate the kind of structural data available for non-crystalline samples from this kind of correlated x-ray scattering measurement, calculated changes in C4 for closed vs. open states of the enzyme dihydrofolate reductas are shown in the Figure 5 [27]. The SAXS profile (left) is similar to the cos (θ) = 0 slice in C4, while changes at large cos (θ) correspond to changes in the internal structure of the enzyme not reflected in the SAXS profile.

Extracting conformational change information from CXS data of the type shown in Figure 7.8 is not trivial, especially in comparing the data to theoretical models. It was noted in the last section that the molecular dynamics simulations are hard to extend to the time scale of millisecond involved in the enzymatic reactions. However, recent success in utilizing Markov state methods (MSM) to simulate protein folding [29] can be potentially used to generate trajectories for enzyme-driven catalysis.

The Pande lab [30] has recently begun application of these methods to study conformational change, such as in cytokine/cytokine-receptor-induced conformational change and the enzyme conformational dynamics of NtrC. MSMs are essentially discrete-time master equations, where the macrostates and rates of transitioning between them are determined from molecular simulation. The Markov states are extracted by kinetic clustering of simulation data. The time dependence of the CXS will be directly predicted by use of MSMs to generate ensembles of intermediate macro-states at atomic resolution.

The expected CXS profile for each of the Markov states will be the fingerprints for the ensemble of possible intermediate conformations expected to be occupied in the catalytic cycle. By analyzing the time dependence of these occupancies in terms of a Markov matrix representation of the data, the matrix elements for connecting one time step to the next in the MSM analysis will be confronted directly with the simulations [27].

## 7.5  Physiology and Biomechanics

The workshop focus panel discussed the growing area of understanding the physiology and biomechanics of small organisms. Explanations of physiological and biomechanical processes seem to arise from combining reductionist approaches with non-equilibrium science. Life depends on non-equilibrium properties of complex interactions that require the constant expenditure of energy to maintain them. In addition, networks of information and control (the nervous system, hormones, etc.) are central to the development, function, and evolution of complex biological systems. Currently, investigations are often limited by the inability to probe inside the organism or a cell or a tissue in real time during the temporal evolution of a behavior or process of interest [31].
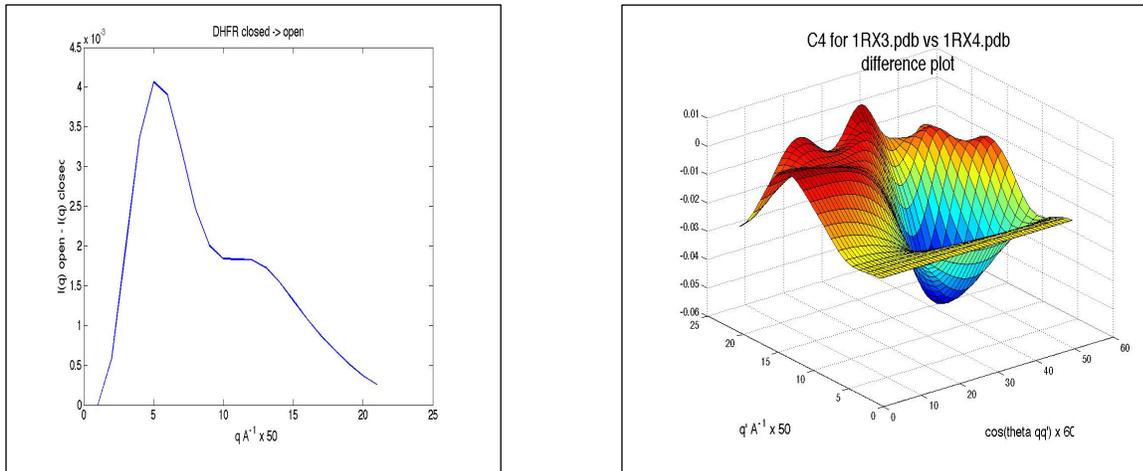
*Figure 7.8  Difference in CXS for two states of dihydrofolate reductase (right) compared to the difference for one-photon scattering (SAXS) for the same pair of states (left) [Courtesy: Sebastian Doniach, 27].*

The range in length scales involved in understanding such complex structures varies from a few hundred microns to sub-nanometers, and the temporal scales of their dynamics will change from milliseconds to sub-picoseconds.

X-ray techniques in general can uniquely provide molecular-level information in muscle tissue under hydrated physiological conditions at the relevant millisecond time scale. It is now possible to perform spatiotemporal studies such as those of the indirect flight muscles in living *Drosophila* during tethered flight [32]. Another such example is the *in vivo* study of cardiac muscle from beating hearts in living animals. These have allowed researchers to relate structural changes to questions of direct clinical relevance [33].

Hemolymph flow patterns in opaque insects have never been directly visualized due to the lack of an appropriate imaging technique. The required spatial and temporal resolutions, together with the lack of contrast between the hemolymph and the surrounding soft tissue, are major challenges. Previously, indirect techniques have been used to infer insect heart motion and hemolymph flow, but such methods fail to reveal fine-scale kinematics of heartbeat and details of intra-heart flow patterns.

Synchrotron x-ray phase contrast imaging is a powerful technique that is generally a direct visualization of dynamics and flow patterns inside opaque animals [34, 35]. This technique has the potential to illuminate many long-standing questions regarding small-animal circulation, encompassing topics such as retrograde heart flow in some insects and the development of flow in embryonic vertebrates. In these studies, *in vivo* intra-heart flow patterns and the relationship between respiratory (tracheae and air sacs) and circulatory (heart) systems were directly observed for the first time. The ability to directly calculate tracheal and air sac volume change from these studies allows more detailed physiological and biomechanical calculations of respiratory function.

The above example only illustrates how important this field will be in the future [33] and how the spatiotemporal x-ray tools, combined with macroscopic measurements will contribute in a major way.

One of the major concerns of this focus panel is radiation damage to biological systems under investigation. Sample damage by x-rays limits the resolution of structural studies on non-repetitive and non-reproducible structures such as individual biomolecules or cells. Cooling can slow sample deterioration, but cannot eliminate damage-induced sample movement during the time needed for conventional measurements. Clever schemes have been developed to overcome the problem. The most prominent among them is the use of femtosecond x-ray pulses [36]. Systematic study of cell cycle checkpoints that ensure the fidelity of cell division in eukaryotic cells is vital. An important function of many checkpoints is to assess DNA damage, which is detected by sensor mechanisms. When damage is found, the checkpoint uses a signal mechanism to either stall the cell cycle until repairs are made or, if repairs cannot be made, to target the cell for destruction via apoptosis (effector mechanism) [37].

Consider the dynamics of internal fluid flows in certain insects, probably one of the most energy efficient processes [38]. Bombardier beetles are armed with a unique defense mechanism that squirts a hot spray of water/steam at $100^0$ C on predators such as ants, frogs, birds, etc. The actual mechanism and chemistry are only partly understood. The non-equilibrium process begins by a squeezing of the muscle of a reservoir containing an aqueous solution of hydroquinones and hydrogen peroxide that is injected into an explosion chamber containing a mixture of catalase and peroxidases dissolved in water (Fig. 7.9).
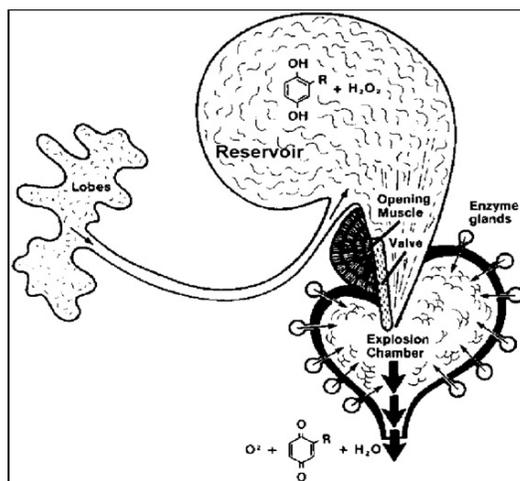


*Figure 7.9  Bombardier beetle discharge apparatus [38;* http://iopscience.iop.org/1748-3190/2/4/001/]*.*

This triggers a fast reaction and the spray through a tiny nozzle that can reach as far as 20 to 30 cm from the explosion chamber, which is only 1 mm in size. This is an ideal spatiotemporal x-ray imaging experiment, which can address major questions:

- Can we fully understand the structure and dynamics of the tissues and organs     that deliver this effective fluid flow?

- Can we create artificial copies of these organs — that evolved over millions of years — for medical and other uses?

- How does a bombardier beetle quickly form nearly boiling liquid in its body and aim a stream in any direction with a velocity of ~ 10 m/s? [32]

- Will this be the model for future fuel injection and spray technologies?

- Can one devise methods to image with x-ray spatiotemporal tools the structure of organs such as the contracting muscles and valves, their motion, and the energy flow processes?

- How can one overcome the interactions of pump or probe pulse with the organism?

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# 8 Focus Panel: Soft Matter Dynamics in Soft Matter and Fluidics

| | | |
|---|---|---|
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## 8.1 Introduction

Soft matter that we come across every day includes copolymeric mesophases, syntheic polymers, glasses, foams, gels, complex fluids, surfactants, colloidal systems, liquid crystals, blood, biomembranes, living tissues, personal care products, fuel sprays, and so on. They all exhibit complex far-from-equilibrium behavior in all their many manifestations as they perform their functions. In spite of their diversity, the energetics involved in all of them is of the order of the thermal energy kT. They can be driven away from the equilibrium phase very easily with weak external forces. Some of the phases may get trapped in configurations that structurally resemble a liquid (they are dense and highly disordered) but are unable to flow and thus behave as solids. The phases may be predominantly in a state of higher entropy that displays new types of structural order not only on the atomic scale, but also on mesoscopic scales (nano- or even micrometers).

Equally fascinating is the behavior of the interfaces between diverse soft matter or between soft and hard matter. The splashing of raindrops on a windshield, the dripping faucet in a kitchen, the cracking of drying paint, the flow of fluids in confined geometries, and adhesion of organic films (lipstick) on tissues (lips) are all examples of intriguing and important phenomena that occur at the interfaces. The dynamics of soft matter as they perform their functions is often determined by the simultaneous contribution of processes occurring on many time scales (from picoseconds to years) and many length scales (sub-Ångstrom to micrometers) [1].

A battery of experimental tools has been developed to measure the complex structures and their evolution in soft matter. They include many spectroscopies and scattering methods such as rheology, Nuclear Magnetic Resonance (NMR), light scattering, dielectric spectroscopy, neutron scattering [2] as well as synchrotron radiation experiments (involving the measurement of x-ray reflectivity, SAXS, GIXD, GISAXS, USAXS, micro- and nano-SAXS, coherent x-ray scattering and imaging, etc.). These have been supplemented by a new class of multiscale simulations utilizing modern molecular dynamics and statistical physics approaches [3].

The focus panel at this workshop limited their deliberations to only a few of the following important questions:

- *How do the interfaces develop as a drop hits a solid/porous surface?*

- *What are the temporal processes in adhesion of glues at molecular level?*

- *What are the fundamental chemical and physical processes involved in supramolecular formation, folding, and phase transitions in block copolymers?*

- *How to probe phenomena such as dynamical self-regulation, clustering, anomalous density fluctuations, diffusion in concentrated suspensions, and rheological behavior?*

- *What are the dynamic processes that lead to hierarchical order in nanoscopic soft materials?*

- *How are the interfaces between different soft-/bio-/hard-matter and in confined geometries formed?*

- *How to understand hydrodynamics of turbulent flows such as those in jets and sprays?*

- *How to understand slow and ultrafast dynamics of surfactant monolayers?*

- *How are the interfacial lubricants between various bio/inorganic surfaces behave in various biological and clinical environments?*

- *How does bio-matter behave in microfluidic environment?*

- *Can we better understand the details of nanofluidic flows encountered in new technologies for separation, sensing, manipulation of molecules and in microfluidic devices for nanoparticle synthesis, micromixing, and cell separation?*

- *Membrane synthesis processes and their functions are integrated from the atomic scale to the macro-scale, which span 7-8 orders of magnitude in length and time scales. How could we follow the pathway of synthesis and functional process?*

The addition of spatiotemporal capabilities (with picosecond- to microsecond- to and sub-angstrom- to micrometer-scale resolution) to the well-developed x-ray spectroscopy, imaging, and scattering techniques mentioned above will allow us to address some of the questions that involve non-equilibrium temporal evolution of structural complexity at the molecular, nanoscopic, and mesoscopic scales.

## 8.2 Dynamics of Granular Material and Bursting Bubbles

The inspiring plenary talk by Sydney Nagel at this workshop set the stage for discussion of this topic in the focus panel. He addressed the complexity and non-equilibrium of systems around us by giving examples such as behavior of anomalous flow of granular material, the long messy tendrils left by honey spooned from one dish to another, the pesky rings deposited by spilled coffee on a table after the liquid evaporates, or the common splash of a drop of liquid onto a countertop.

At a scientific level many questions have come up. What happens when one drops a steel ball into fine sand? It turns out that one gets a granular post-impact "splash." What is the nature of the flash when a liquid drop hits a solid surface or a liquid surface? The process of splashing on the surface was generally thought to be initiated by a rapid shock and subsequent ejection of a sheet that displayed a variety of splashing patterns [4]. Modern optical techniques (interferometry, evanescent wave microscopy, etc.) with microsecond and sub-micron resolution of splashing drops on surfaces have given many insights on the process. When a steel ball hits loose sand, it is quickly engulfed and a surprisingly vigorous jet shoots upward from the surface of the sand [5]. In a similar way, as a liquid drop approaches the solid or liquid surface (at a distance of < 100 nm) a thin film of air is formed that separates the liquid from the surface, forcing the drop to spread laterally upon impact. A complex sequence of events ruptures the air interface and ultimately produces a contact between the drop and the surface; the initially smooth air film generates discreet holes at the interface that are then filled by the liquid or sand. These holes rapidly spread and coalesce into patterns such as a ring of wet surface surrounding a trapped bubble of air [6]. However, splashing is completely suppressed if the surrounding gas pressure is lowered [7, 8].

What will be the role of hard x-rays in understanding the processes surrounding splashing? The experiments that contributed new information on the subject used x-ray absorption techniques. The first study was of a falling steel ball on loosely packed sand [9]. Utilizing the high-intensity x-ray beam from the Advanced Photon Source, an x-ray absorption movie was created at a rate of 5000 frames per second. The movie showed the formation and ejection of the granular jet. Figure 8.1 shows image sequences assembled from experimental runs for a 12-mm steel ball in a 30-mm-diameter cylindrical container at atmospheric pressure, where the effects of the interstitial gas are most pronounced. In Fig. 8.1a, the cylindrical void created at the first impact of the ball is shown. The sand walls then collapse radially into the void and collide along the central vertical axis. The rate of wall collapse initially increases with depth below the surface. With the first point of contact between the ball and the sand surface, a small upward jet is developed (see Fig. 8.1c). The thick jet (in Fig. 8.1 c-e) is developed subsequently in the processes that are driven by the air interface at the point of first contact.

The role of the air interface is common to many situations involving splashing of an object on a solid or liquid surface. For example, a liquid drop falling on a solid surface generates an air bubble at the interface
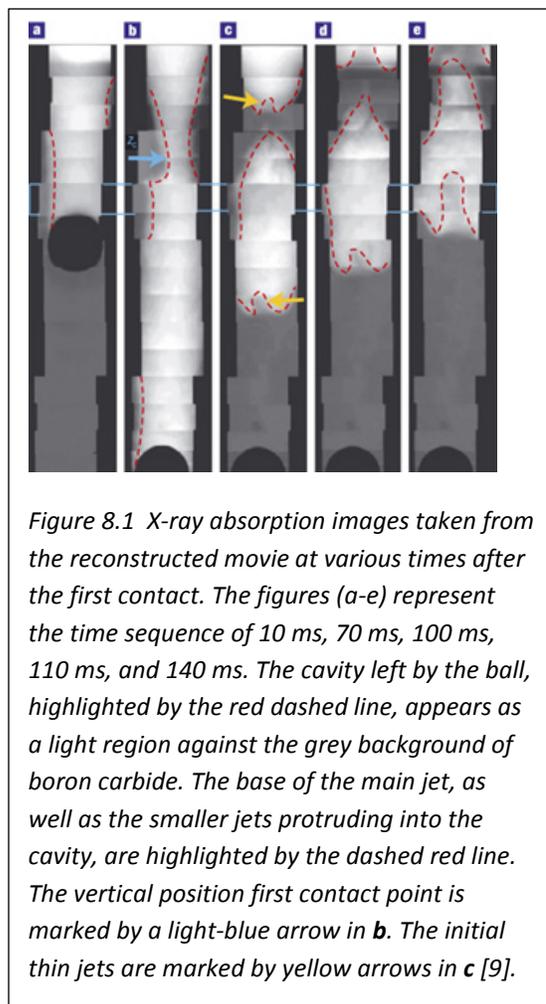


Figure 8.1  X-ray absorption images taken from the reconstructed movie at various times after the first contact. The figures (a-e) represent the time sequence of 10 ms, 70 ms, 100 ms, 110 ms, and 140 ms. The cavity left by the ball, highlighted by the red dashed line, appears as a light region against the grey background of boron carbide. The base of the main jet, as well as the smaller jets protruding into the cavity, are highlighted by the dashed red line. The vertical position first contact point is marked by a light-blue arrow in **b**. The initial thin jets are marked by yellow arrows in **c** [9].

that shows complex evolution of the structure in time. These are multi-parameter problems involving ambient air pressure, drop size, viscosity of fluids involved, etc. Some of the optical studies have given excellent insight into the temporal development of the process. Recent x-ray absorption movies [10, 11] have given both required spatial and temporal resolutions to quantitatively address the non-equilibrium hydrodynamics. The spatial definition in these images is enhanced by the phase contrast generated by the coherence of the x-ray beam. Figure 8.2 shows phase contrast x-ray absorption images of the spatial and temporal evolution of an air bubble bursting at the interface of a falling ethanol drop and a glass substrate [10]. The general conclusions of these bubble-bursting measurements are common to many systems and processes and point to the important role of the air film between the drop and the surfaces.

Bubble bursting is the key process involved in atmospheric aerosol production and the scavenging activity of biological materials, for physical oceanography, atmospheric chemistry, weather and climate modeling, chemical engineering, and human health. The bubble size limits the jet formation from bursting bubbles in low-viscosity liquids and has been verified with ultrafast x-ray phase-contrast imaging for bubbles with small radii ($R < 100$ μm). This finding will be useful in controlling the bursting

process in refreshing drinks by changing the surface tension, viscosity, or density, perhaps achieved by adding surfactants or functional ingredients.
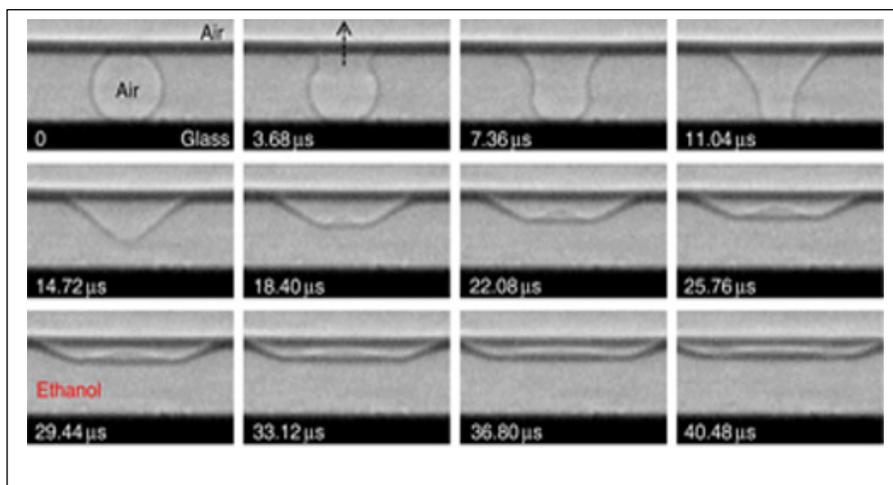


*Figure 8.2 X-ray phase-contrast imaging reveals surface evolution of bubbles beneath liquid utilizing the high penetration capability of x-ray photons. The constant falling height (35 mm) in the drop-impact experiments generated bubbles with the same volume, regardless of the liquid or substrate. Ultrafast x-ray imaging of a bursting bubble (R=24.5 μm) in ethanol on a glass substrate. The images show no jetting for such a small bubble [10].*

At a fundamental level, there are several distinct regimes in the splashing of a drop on a smooth, dry substrate. Although low-viscosity and high-viscosity splashing appear to be markedly different, they both exhibit two separate regimes of behavior at high and low impact velocity. The splashing and bubble forming phenomena on a liquid surface adds to the parameter space [11]. As parameter space continues to be explored, even more splashing regimes may be found. The studies utilizing x-rays [10, 11] open new opportunities for a detailed quantitative understanding of spatiotemporal evolution of coalescence of two droplets, aerosols, and jets.

## 8.3  Hydrodynamics of Flowing Fluids: Micro- and Nanofluidics

Fluids in general include suspensions, emulsions, foams, polymer melts and solutions, surfactant solutions, and biomolecules. Flows of these complex fluids display far-from-equilibrium phenomena that are not found in simple fluids, including interfacial and bulk instabilities, texture formation, and evolution [12]. A more complete review of the subject is available in a special volume of *Chemical Society Reviews* [13].

Flowing fluids also present the most common phenomena in nature as well in technology applications. Examples include transport of fluids in confined geometries including man-made micro-machines, medical devices, zeolite pores, the human body (cardiac and cardiovascular systems, pulmonary system, tissues, etc.), membrane polarization filters in desalination of sea water, and gasoline injectors in

combustion engines. The applications of transport in nanochannels range from pumping and transport control, to energy conversion and separation. In the energy industry, one always asks how to make the oil flow. The processes used in extraction of oil from the ground or deep sea include water or gas injection, steam, microwave, or underground combustion to facilitate the flow, and the use of polymers to loosen trapped oil. The ultimate processes involved are the extraction and flow of complex fluids through pores. Any of these old or new technologies should also include a "green environment." The high surface-to-volume ratio in all these applications plays a dominant role, causing the transport to be determined by interactions between the liquid and/or molecules inside it, and the walls. Fluid flow at the microscale and nanoscale exhibits uniquely differing physical phenomena: the flow could be lamellar or turbulent, consisting of large or small number of molecules in micro or nanochannels, giving rise to the continuum and discrete modeling utilizing computational fluid dynamics [14].

The micro- and nano-fluidic flows are often turbulent and are far from their equilibrium. It would be necessary to perform measurements of the dynamic processes in confined flows with nanoscopic- and molecular-resolution tools on the spatiotemporal scales of sub-nm to 1000 nm and from femtoseconds to microseconds. The biggest challenge in the next decade for the experimentalists is to develop new approaches and novel tools, and for the theorists to selectively apply Stokes and Nernst–Planck equations to appropriately describe the confined fluid flow systems. Both the experimental work and theory should involve computational scientists, chemists, biologists, engineers, and technologists.

### 8.3.1  Fuel Spray and Soot Formation

Turbulence and multiphase flow remain among the most demanding areas of both experimental and computational physics [15]. A familiar example is in understanding the dynamics of high-pressure, high-speed fuel sprays in a combustion chamber, which is not only an intellectual challenge but also crucial to increasing engine fuel efficiency and reducing engine-produced pollutants (See Box 1). The process of fuel-jet break-up leading to atomization begins at the nozzle exit. The shape, size distribution, and dynamics of the droplets in the diverging spray away from the nozzle exit are strongly dependent on the nozzle internal design, initial flow conditions, and Weber number. The challenge is to obtain a full spatiotemporal description of the spray from its birth to ignition and to describe it fully by utilizing hydrodynamic computational models. Because liquid sprays are difficult to image with commonly employed optical imaging and scattering methods (particularly in the region close to the nozzle), high-pressure fuel sprays have never been considered as supersonic under typical fuel-injection conditions, although the modeling of such sprays predicted that the fuel jets can exceed supersonic speeds and result in gaseous shock waves [16]. This is an area where x-ray imaging methodologies have already made a major impact [17].

Detailed measurements on the breakups of high-pressure sprays and mass distribution close to the nozzle in regimes beyond the capillary wave-controlled low-velocity domain have not been possible with optical techniques [18]. The utilization of x-ray tomographic images has provided needed insight into the fundamental breakup phenomenon associated with the hollow-cone gasoline spray in the near-nozzle region [16,19]. The x-ray absorption images of temporal evolution of the gasoline spray in the near

nozzle-region with microsecond resolution is shown in Fig. 8.3. In this measurement, the fuel injection was set to 135 MPa, resulting in maximum leading-edge speeds of 345 m/s that developed a shockwave front (Mach cone) that can be seen the figure.
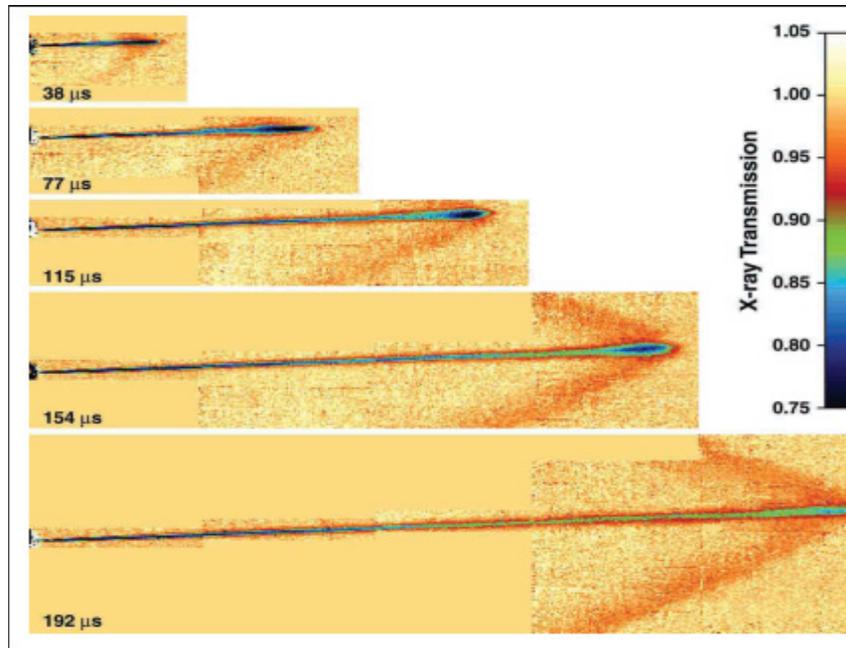


*Figure 8.3  Time-resolved x-ray absorption images of fuel spray and shock waves generated by the sprays at various times (shown in the images) after the start of the spray injection, Courtesy Jin Wang (*doi:10.1107/S0909049504032297*)[19].*

The time-resolved quantitative fuel distribution measurements allowed a realistic numerical fluid dynamic simulation with initial conditions based on the measurement, which demonstrates that the fuel has completed the primary breakup upon exiting the nozzle. The secondary-breakup-based simulation also agreed well with the experimental fuel-volume fraction distribution, which challenges most existing simulation assumptions and results [20].

A closely related area of investigation is soot formation in an incomplete combustion of hydrocarbon fuels [21]. Soot is produced in fuel-rich environments where there is insufficient oxygen for hydrocarbon fragments to be completely oxidized. Instead, these small, largely unsaturated hydrocarbon species bond together to produce larger molecules which continue to grow until they become soot. Fuel jets in diesel and jet engines are perfect incubators for soot study of soot formation is even more important in order to develop methods to reduce the health hazards associated with soot production, improve the radiative transfer of energy in industrial applications, and devise efficient production processes that use

# Box 1: Spray Dynamics and Chemistry of New Fuels

*"The evolution of fuel spray plays a defining role in controlling the efficacy of ignition and the uniformity of combustion, and hence in determining both the combustion efficiency and the formation of soot and toxic partially oxidized and unburned hydrocarbon pollutants emitted into the exhaust stream. The physics and chemistry of this multiphase problem are difficult to probe experimentally, to understand theoretically, and model rigorously. This problem is particularly critical in the design of new engines for emerging fuels because key processes such as the physical breakup of the liquid spray, the mixing of vaporized fuel with the cylinder gases, and the chemistry at droplet interfaces under high pressure will change—in ways that cannot at present be reliably predicted—with the new chemical and physical characteristics of non-traditional fuels…………"*

*"…….In a traditional spark-ignition (SI) engine, the combusting fuel-air mixture is very close to stoichiometric, which results in high temperature conditions and significant NOx formation. In a traditional Diesel engine, there is little time for fuel and air to mix before combustion, therefore there is a range of fuel-air mixtures when combustion starts.*

*The fuel rich combusting regions in a Diesel form soot while the stoichiometric combusting regions form NOx. Novel combustion concepts being explored for high-efficiency, low pollutant emission engines are based on strategies for achieving Low-Temperature Combustion (LTC). Novelcombustion concepts being LTC requires the formation of reacting mixtures in an engine that are dilute enough to not produce the high temperatures that lead to NOx (thus the reference to low-temperature combustion)and that have well enough mixed fuel and air to avoid soot formation. …………..*"
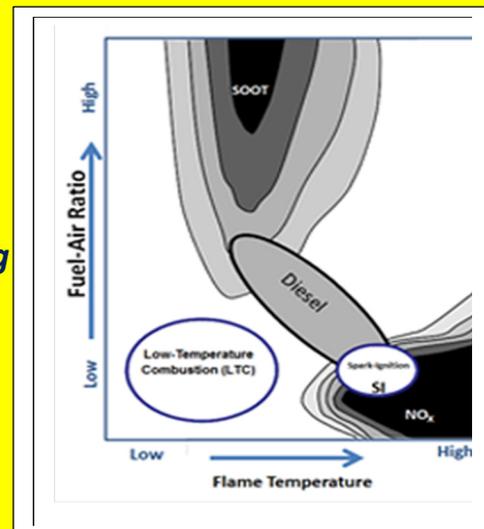
soot in various applications. Understanding the formation of a single soot particle or a droplet at atomic resolution is a grand-challenge problem. Small-angle x-ray scattering is a useful tool to investigate *in situ* the morphology of soot in the region between 1 and 100 nm and complements the *ex situ* technique of electron microscopy. SAXS studies have been employed to measure the initial distribution of soot particles in flames formed by various fuels [23] that shed light on pyrolysis and oxidation. These SAXS profiles have been reduced to give the mean radius and dispersion of a distribution of spherical particles. Mean radii between 0.8 and 18 nm have been observed, demonstrating the power of the tool.

### 8.3.2  Food Absorption through Butterfly Proboscis: Fluid Flow in Flexible Microfluidic Channels

The ability of butterflies to drink nectar from floral tubes raises the question of whether the conventional view of the proboscis as a drinking straw can account for the fluid. The feasibility of performing *in situ* time-resolved SAXS studies to understand the dynamics of soot nanoparticle growth in flames with sub-ms resolution has been reported [24]. The method allows direct two-dimensional mapping of soot nucleation and growth in a flame of size distribution 0.5 to 500 nm with a time resolution of less than 100 μs, depending on the gas flow rates. Simple diffusion-controlled growth laws have described the results, although a more computationally intensive modeling will be required in the future. To shed light on the basic physical and chemical principles involved in their formation in real environments, control of soot size and better time resolution will be required.

Predictive modeling is critical to this field of research, which will deliver the spatial and temporal accuracies that can be measured with the available experimental tools of hard x-rays. There is intensive effort in simulation and modeling utilizing the prowess of high-end, petascale, "leadership-class" computing facilities, such as the DOE SciDAC and INCITE programs [26].

can be considered as a flexible microfluidic device with an extraordinary ability to probe, deliver, and sense different fluids. Proboscis evolution, organization, and functionality are poorly understood, though its design is attractive for making artificial probes for single-cell analyses. X-ray phase contrast imaging is the tool of choice [27] to observe the process of fluid imbibition into the food canal with the required spatial and temporal resolution [28].

A study performed on the proboscis of a monarch butterfly utilizing split-field geometry is shown in Fig. 8.4a. Detailed analysis of a series of phase contrast x-ray images obtained during the flow process has concluded that a butterfly proboscis is a complex fluidic system with at least two levels of channel hierarchy. The proboscis represents a sponge and a drinking straw in a single embodiment. The sponge part of the proboscis contains nanopores to provide strong capillary action to absorb the fluid. This is connected to micropores that facilitate the fluid flow through a straw-like channel. Fluid moves into the food canal, forming a film that enlarges into a bulge (Fig. 8.4b). The liquid bulge enlarges until it collapses into a liquid bridge due to plateau instability. Liquid bridges are formed by collapsing bulges as the surface energy reaches an optimum. The flow canal, in conjunction with the sucking pump, represents a second microlevel structure. The pump transports the fluid from the bridges to the gut. The x-ray images show all the details of the proboscis: the pump, the gut, and the formation and collapse of bulges, a process that occurs over the sub-second time range.

This pioneering study on the flow of fluids through porous and fibrillar structures is perhaps common to the all insect groups (such as flies, moths, and bees). Nature's strategies provide a transformative two-step model of capillary intake and suctioning utilizing integrated nano- and microfluidic structures. In the future, the complexity of fluid flow showing the essential role of capillary action in acquiring liquids at a cell level from porous substrates can be visualized with nanometer-resolution x-ray phase contrast imaging methods. Can we develop bioinspired nanofiber structures similar to the proboscis for various applications?

### 8.3.3 Hydrodynamic Interaction of Flowing Colloid Suspensions

Liquid suspensions containing colloidal particles of nanometer-to-micron size (colloids) are ubiquitous in industry and biology [27]. There too are many industrial experiences to enumerate, such as paint spray devices, ink cartridge spray, effective spraying of insecticides, nano-fluidic devices suitable for medical applications, and blood flow through vesicles – even cleaning the oil spill in the Gulf of Mexico utilizing surfactants. Fluid flow in micro- and/or nano-patterned channels is a growing field that addresses the design of micro-/nano-channeled devices with specific applications [28].

In liquids containing colloidal suspensions, the hydrodynamic interactions between suspension particles are positive (particles drag one another in the same direction), long-ranged (decaying with inter-particle distance as $1/r$), and involve many-body effects (i.e., depend on concentration). The spatial distribution of the colloid particles in a fluid, termed the microstructure, is set by the balance of forces in equilibrium. In microfluidics, it is generally accepted that the hydrodynamic interactions are screened [29]. For example, in a narrow channel with quasi-one-dimensional geometry, the coupling decays with r/w, where w is the channel width. In a quasi-two-dimensions geometry of the micro-channel, the coupling between particles remains long-ranged $(r/H)^{-2}$, where H is the gap between the flat walls. These situations are generally associated with low Reynolds numbers, making the interactions linear. Under the right conditions, colloidal suspensions can show various types of order. They can undergo a glass transition as particle density is increased and the particle volume fraction exceeds 0.6 [30]. Near this colloidal glass transition, the system can be trapped in metastable states (known as crowding and jamming) [31]. These static metastable orders have been a subject of intense x-ray investigations utilizing both XPCS and SAXS techniques [32].
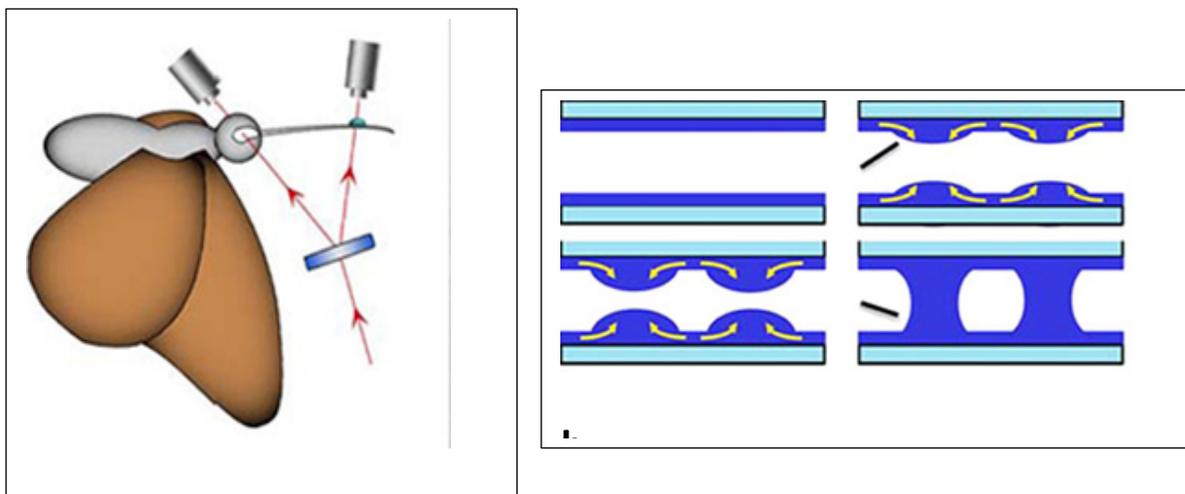
*Figure 8.4  a. X-ray phase-contrast imaging of the monarch butterfly proboscis and formation of liquid bridges. (a) Schematic displaying the split-beam (arrows) X-ray phase-contrast imaging used to simultaneously view liquid-bridge formation in the proboscis and action of the sucking pump, utilizing cameras two cameras simultaneously. (b) Schematic of meniscus formation. Fluid moves into the food canal, forming a film that enlarges into a bulge until it collapses into a liquid bridge due to excessive surface energy. Arrows show fluid motion (from Ref. 28).*

In colloidal systems, the primary interest in the flow dynamics arose from an experimental need to reduce radiation damage from the x-ray exposure of soft matter. Combining x-ray techniques with microfluidics as an experimental strategy reduced the risk of x-ray-induced beam damage [33]. On the flip-side, microfluidic methods allowed time-resolved studies of processes taking place in flow cells that often involve the non-equilibrium regime. Under imposed flow, the ability of the microstructure to rearrange to accommodate flow and interparticle forces determines its macroscopic rheological response. At low shear rates, Brownian forces are able to restore shear-induced perturbations to the equilibrium microstructure on the time scale of the shear flow. As the increased shear rate (or flow rate) becomes comparable to the Brownian forces, one achieves shear thinning (Fig. 8.5). Higher shear rates lead to hydrodynamic interactions that can induce particles to orbit one another, disrupt the particle network, and create qualitatively a new regime of shear thickening. Eventually the particles organize into hydroclusters [34]. A confined geometry (nano-to-micrometer) will further complicate the observations.

Before utilizing the coherent x-ray scattering techniques (XPCS, SAXS, CDI) to investigate non-equilibrium flow systems, closer analyses of the shear state, effect of confinement, and relaxation processes in the system being investigated are required. In non-equilibrium systems, the average x-ray scattered intensity varies with time and it is necessary to separate fluctuations from a changing average (which is measured in the equilibrium state). In addition, the variation in velocity across the scattering volume affects the intensity autocorrelation function. So the correlations may not depend only on the time difference, and a full two-time correlation function may be needed [35]. Of course, if the fluctuating component is much faster than the variation in the average, a quasi-equilibrium approach may work.
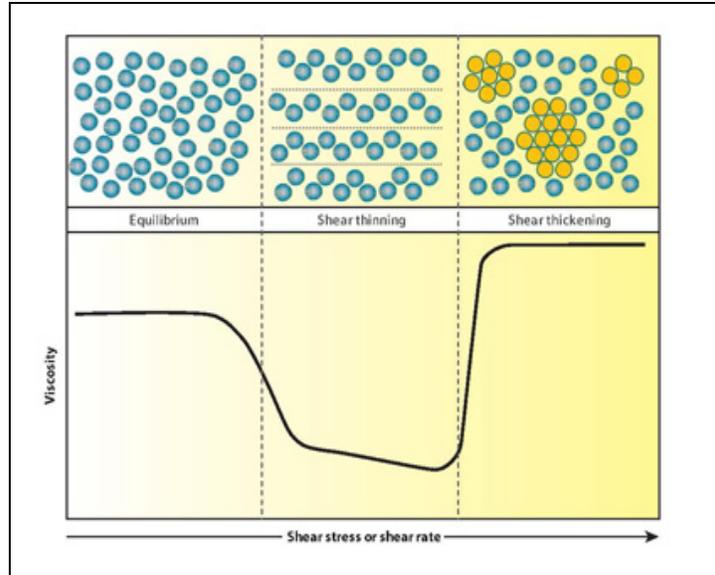
*Figure 8.5  The relationship between microstructure and viscosity of the shear thinning-shear thickening transition in hard-sphere colloidal suspensions. In equilibrium, random collisions among particles (blue spheres) make them naturally resistant to flow. However, as the shear stress (the shear rate) increases, particles become organized in the flow, which lowers their viscosity. At yet higher shear rates, hydrodynamic interactions between particles dominate over stochastic ones, a change that spawns ordered clusters (orange spheres) [from Ref. 34].*

There are many examples in which flow dynamics have been investigated utilizing coherent x-ray scattering techniques. We will illustrate the current research directions with two examples discussed at the workshop.

The colloidal system can be investigated utilizing XPCS along the length of the flow cell whether it is inhomogeneous (pressure-driven) or homogeneous flow. In a transverse flow, with the scattering being perpendicular to the flow direction, the measured correlation functions are mostly sensitive to the diffusive motion of the scatterers. On the other hand, in a longitudinal flow geometry the correlation functions are strongly affected by the rheological properties of the flow (shear profile). In a highly dilute colloidal suspension of sterically stabilized colloidal silica spheres with a Reynold's number of $10^{-6}$, the native diffusive motions in the sample may be separated from effects associated with the applied flow [36]. The decay of the homodyne intensity autocorrelation function from the XPCS measurements reflects three relaxation processes: particle diffusion (D), as in conventional equilibrium dynamics with dilute collides; de-correlation as particle transit (T) through the scattering volume; and shear-induced (S) oscillatory decay that reflects the variation in particle velocity within the scattering volume. The normalized intermediate scattering function, $g_1(\mathbf{q},t)$, can then be separated in to three parts, each representing the three processes [33, 36]:

$$|g_1(\mathbf{q},t)|^2 = |g_{1,D}(\mathbf{q},t)|^2 \cdot |g_{1,T}(\mathbf{q},t)|^2 \cdot |g_{1,S}(\mathbf{q},t)|^2.$$

Often the second decay (T) process is long compared to other contributions observed in most XPCS measurements.

Future emphasis in this field will include investigations of biological systems such as cells and cellular components where the governing length scales are nanometer to micrometer. It may be inferred from the studies of colloidal systems that the x-ray scattering and diffraction techniques could also be useful for the study of biological processes where the spatial and time resolution extends well into the relevant scales. At the same time, the investigation of such systems in both areas of research requires well-defined and controllable sample environments. One way to establish such environments for biophysical studies is by extending continuous-flow microfluidic devices tailored for a particular experiment. An early example is the work of Pollack et al. [37], who investigated the dynamics of protein and RNA folding by SAXS utilizing channels etched in silicon wafers and topped by thin polydimethylsiloxane (PDMS) films. In these studies, the device dimensions and flow rates are chosen such that a complete diffusive mixing of the solutions can be achieved in minimal time.

Investigation of flow and assembly dynamics, as well as kinetics of proteins into aggregates or fibers requires defined chemical environments. Choosing a suitable geometry of the reaction cell and the ability to control the flow rates of the reactants is critical to these investigations. The example discussed at this workshop involved formation of cytoskeletal intermediate filaments (IF) from vimentin IF proteins [38]. In the example, multilayer photolithography was utilized to fabricate flow cell. The layout of the mixing cell is shown in Fig. 8.6, where the biomacromolecules and smaller reactants can provide laminar diffusive mixing and well-controlled gradients. Tetrameric vimentin protein solution entered the device from the central inlet and the salt buffer from the sides. The buffer hydrodynamically focused the vimentin solution to a jet. As the flow continued down the main channel, the salt diffused into the vimentin solution and started the assembly process. To prevent the adsorption of assembled vimentin to the channel walls, it was necessary to cover the vimentin with salt buffer from all sides as soon as it entered the intersection.

SAXS is a very useful tool for investigating the filament assembly process and the intermediates. The small size of the x-ray beam in comparison to the mixer dimensions allowed probing of the assembly process in time, from the spatially resolved measurements along the length (x-axis in Fig. 8.6) of the microfluidic mixer. Because of the constant flow in the device, probing at a position further downstream corresponded to probing a later assembly time. A further advantage of the constant flow was the continuous exchange of material that minimized radiation damage from the x-rays.

In Fig. 8.7, the measured SAXS patterns measured along the length of the microfluidic mixer are shown. The Kratky plot of SAXS data (Fig. 5.8c) collected at different positions in the jet corresponding to different salt concentrations (shown in Fig. 8.7a) along with modeling reveals distinct differences between the earliest assembly states. There is a rapid increase in the radius of the macromolecular assemblies, with the mean square radius of gyration perpendicular to the filament axis upon assembly. This example provides dynamic structural data of a complex assembly of cytoskeletal intermediate filaments from vimentin proteins.
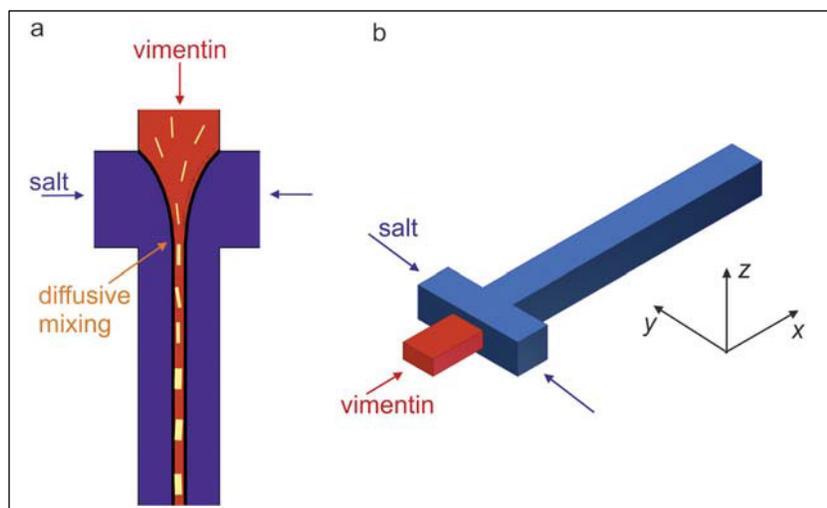
*Figure 8.6  Layout of a microfluidic laminar flow mixer, Courtesy Sarah Köster ([DOI: 10.1039/C0LC00319K](DOI: 10.1039/C0LC00319K)) [38]*

### 8.3.4  Nonlinear Electrorheological and Magnetoreheological Fluids

Electrorheology (ER) and agnetorheological (MR) fluids denote the control of material flow properties (rheology) through the application of an electric or a magnetic field. ER or MR fluids generally consist of solid particles of dielectric or paramagnetic material suspended in electrically insulating oil that exhibit a viscosity change under an electric or a magnetic field. Suspensions of polarizable particles in non-polarizable solvents form fibrillated structures in strong electric or magnetic fields.

The resulting increase in viscosity of these ER and MR fluids can couple electrical or magnetic components to hydraulic components in a servomechanism. The physical properties of these fluids are unusual owing to the long-range, anisotropic nature of the inter-particle forces. Immediately after the electric field is applied, elongated chains or columns of particles align parallel to the field. This structure then coarsens as a result of thermal forces between the columns. Sheared fluids show yielding behavior at low stresses followed by shear-thinning behavior at higher stresses, as discussed in the last section (see Fig. 8.5).

If the electric or magnetic field exceeds a critical value, the fluid turns into a solid whose yield stress increases upon increasing the field. Within the general assumption that the dielectric and conductive responses of the component materials become non-linear in the stressed state of a typical ER fluid, an upper bound for the yield stress is estimated to be about 6 kPa. The phase behavior of these systems is determined to first order by a dipole-dipole interaction that favors head-to-toe dipole orientations. Hence, with an increasing field the particles tend to form aggregates, strings, and columns aligned along the field direction. With further increase in field, one realizes hcp order, and finally, a high-field ground-state structure that is either a liquid-bct coexistence-phase or a bct phase (mesocrystallites) [39]. Some of the nanoparticles suspended in suitable fluids, mixed with molecular liquids such as water, have demonstrated yield stresses well above 250 kPa or even higher under large electric fields with a reversible liquid-solid transition and a time constant of ~ 1 ms [40, 41].
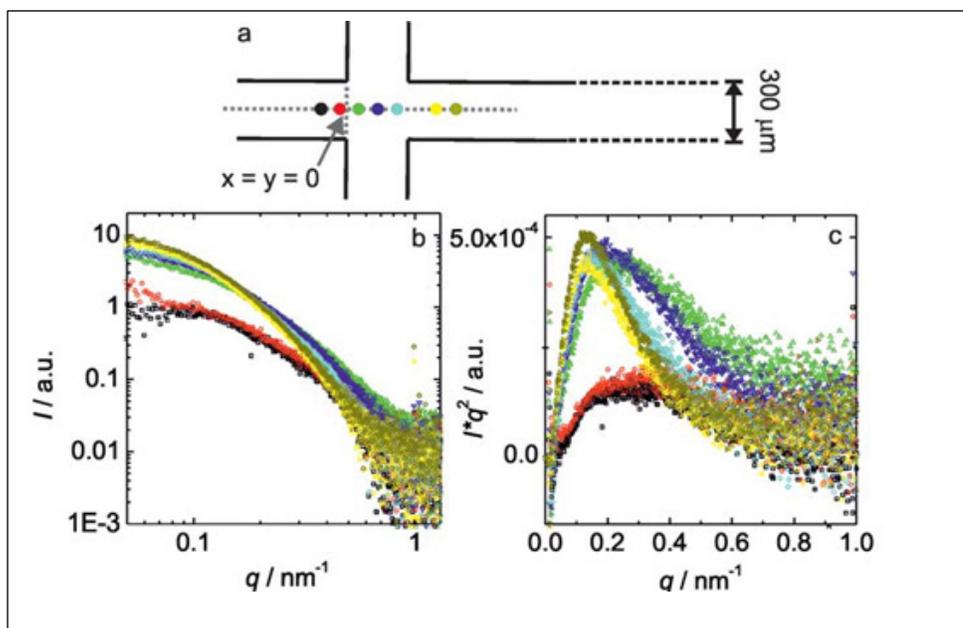
*Figure 8.7 Small-angle x-ray scattering data from various positions in the flow along the length of the mixer. a) Sketch of the cross and measurement positions. The same color code is used in b) and c). b) Log-log plot of the scattering curves. After an initial increase the curves continue to become steeper at positions further down the flow. c) Kratky plot of the same data. Three different types of curves that can be clearly distinguished represent various assembly states, Courtesy Sarah Köster (DOI: 10.1039/C0LC00319K) [38].*

These modern giant electrorheology (GER) fluids with enhanced yield stress make them suitable for numerous applications requiring active control such as brakes and clutches in automobiles or jet planes, or crystals for photonic applications.

In Fig. 8.8, the measurement of yield stress as a function of applied field is shown for nanoparticles of $Ba_{0.8}(Rb)_{0.4}TiO(C_2O_4)_2$ coated with urea dispersed in silicone oil [42]. The nonlinear response of the system to different particle sizes is remarkable. A clear difference in the ER effect on the particle size can be seen, with the smaller particle attaining a larger maximum yield stress of over 250 kPa at 5 kV/mm electric field. The ER and MR fluids containing nanoparticles offer a whole range of new phenomena in non-equilibrium condensed matter physics. What is most interesting is the dynamics of phase ordering, phase changes, and nonlinear interactions under the influence of external fields.

The coherent properties of the hard x-ray beam will help in the study of both static and dynamic effects in the linear and nonlinear phases, dependence on particle size, and on volume fraction [43]. While most measurements thus far have delivered spatial averages, performing spatiotemporal measurements will provide a true clue to the time evolution of the order in different nano-volumes of the fluid the electric field is applied or removed. The use of 2-D and 3-D TR-tomography, pump-probe XPCS (measuring two time correlations), and TR-SAXS sampling small volumes of the fluid with nanoscopic resolution will stand out as important tools for future investigation along with physical modeling of rheological fluids

utilizing modern computational tools [44, 45]. Use of a fluctuating electric field on rheological fluids will open both new phenomenon and newer applications. The spatiotemporal relaxation processes [46, 47] between various phases of ER and MR systems would form inviting problems for the x-ray tools probing non-equilibrium dynamics.
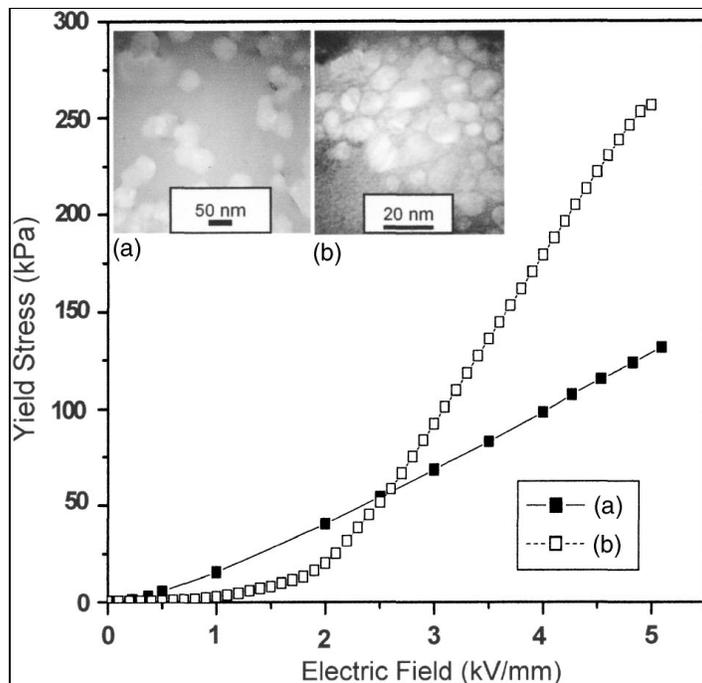


*Figure 8.8  A comparison of the ER effect variation with the electric field for GER fluids with different particle sizes but the same concentration in the fluid. Inset: TEM images of coated nanoparticles. Te nanoparticles were fabricated without (a) and with (b) Rb to the core materials [42].*

## 8.4  Complex Pathways of Self-Assembly Processes in Soft Matter

Soft matter displays a vast number of equilibrium microstructures that includes spherical, cylindrical, or disklike micelles, bicelles, vesicles, and lamellar, cubic and hexagonal phases [48, 49]. The very origin of this structural diversity in membranes, soft colloids, or elastic rods and macromolecules arises from its very low shear modulus, roughly 9-12 orders of magnitude smaller as compared to hard matter. Even minor shear flow can drive soft matter systems far away from equilibrium. As the system recovers from the sheared phase, it has many pathways for self-assembly that can derive many equilibrium or quasi-equilibrium microstructures. The deformation of a soft object depends on the flow that changes hydrodynamic boundary conditions in an intricate and non-linear fashion, since the object shape acts back on the flow field via hydrodynamic screening. Unraveling the complexity of these pathways of self-assembly is a grand challenge from a fundamental view point. In addition, deeper insights about the underlying dynamics could offer predictive capabilities in the bottom-up approach for a wide range of synthesis routes and applications in bio- and nanotechnologies [49]. It would be even more interesting

to identify strategies to manipulate dynamic variables to define a desired pathway by feedback control schemes, for example by restraining shear stress, concentration, or rate of mixing.

One of the text-book illustrations of the evolution of complexity in transient intermediate structures is the self-assembly process of unilamellar vesicles (ULVs) [50], which are of potential use in nano- and biotechnology. They are considered model systems to represent cell membranes. Spontaneous self-assembly was initiated by rapid mixing of the surfactant solutions of anionic lithium perfluorooctanoate (LPFO) and zwitterionic tetradecyldimethylamine oxide (TDMAO). The temporal evolution of transient intermediate structures was probed with a stopped-flow device by TR-SAXS. Inthe study, the mixtures forming unilamellar vesicles were varied over a wide range of concentrations and mixing ratios. A typical data set of SAXS intensities as a function of x-ray wave-vector is shown in Fig. 8.9. This was measured at various times after the non-equilibrium state was established in the stopped-flow device after rapid mixing of the two surfactant solutions of specified concentration.

The solid lines through the data represent simulation of the x-ray scattering function for various shapes of the microstructureThe model mainly predicts disk-like transient intermediate structures with a mean radius of approximately 6.0 nm and bilayer thickness of about 4.0 nm. Beyond about 200 ms, disk-like micelles grow in size and finally close to form unilamellar vesicles. It is observed that with increasing concentration, a more elongated cylinder-like form resulted, and torus-like micelles evolved at lower concentrations. Thus, one may control the outcome of the self-assembly by following various pathways, starting with different concentrations as illustrated in Fig. 8.10 [50].

In this example, the final structures can be obtained via quite different structural pathways. This opens opportunities to manipulate the time scales and the formation process itself by appropriately choosing the system composition. Most important, this is a classic demonstration of the evolution of complexity and its control in soft matter. Improving the characterization tools — such as described above — of static, dynamic, and *in situ* self-assembly remains a current and significant challenge. Self-assembly of large biomolecules and biomolecular assemblies in a hydrated and non-crystalline state poses a tremendous experimental challenge. However, a novel laminar microfluidic jet with diameters in the range of 10–50 μm and operating at shear rates in the range of $\sim 10^6$–$10^8\,\mathrm{s}^{-1}$ can be utilized to produce partially oriented biomolecular assemblies [38]. These self-assembled molecules are adequate to measure their structure in their aqueous environment utilizing XFEL sources or the high-brilliance storage-ring x-ray sources and coherent diffraction imaging (CDI) techniques [51].

New x-ray tools are required in future, such as the 3-D tomography or new coherent diffraction imaging tools that are becoming available both at the third-generation x-ray facilities and the x-ray FEL facilities to bridge the gap between electron and optical tools [52]. Furthermore, the physics- and chemistry-based multiscale models will play a central role in analysis of the x-ray scattering data as well as in understanding the evolution pathways to various microstructures.
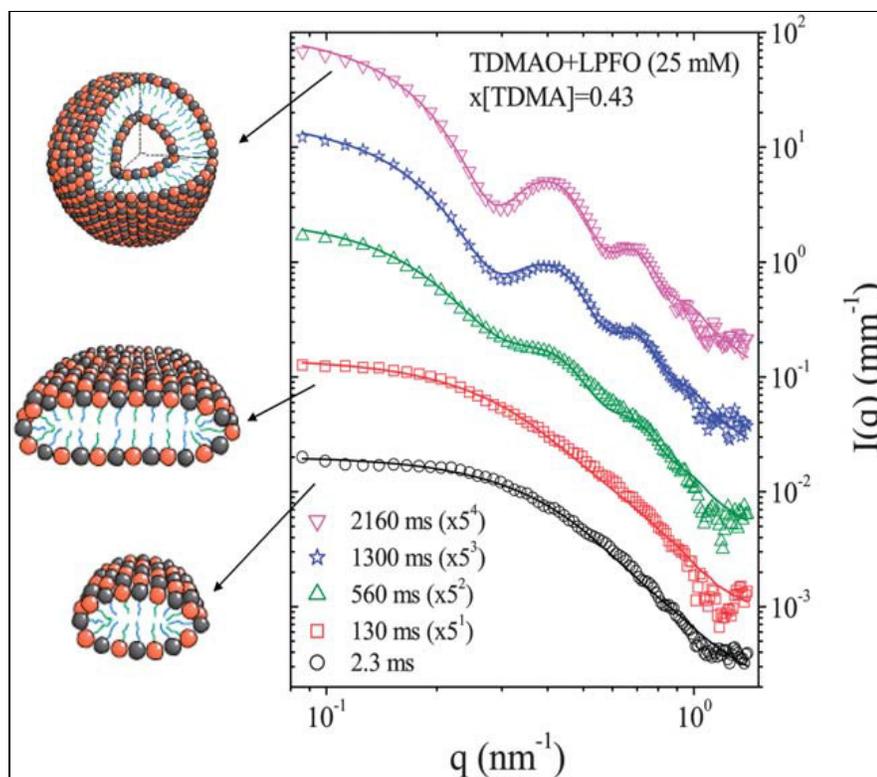
*Figure 8.9 Representative time-resolved SAXS intensities after mixing of 25-mM solutions of TDMAO and LPFO with x [TDMAO] (x=0.43). Successive curves have been multiplied by a factor of five for clarity. The continuous lines correspond to various microstructure models. The cartoons illustrate the different aggregate shape, Courtesy Theyencheri Narayanan(DOI: 10.1039/C1SM05354J) [50]*
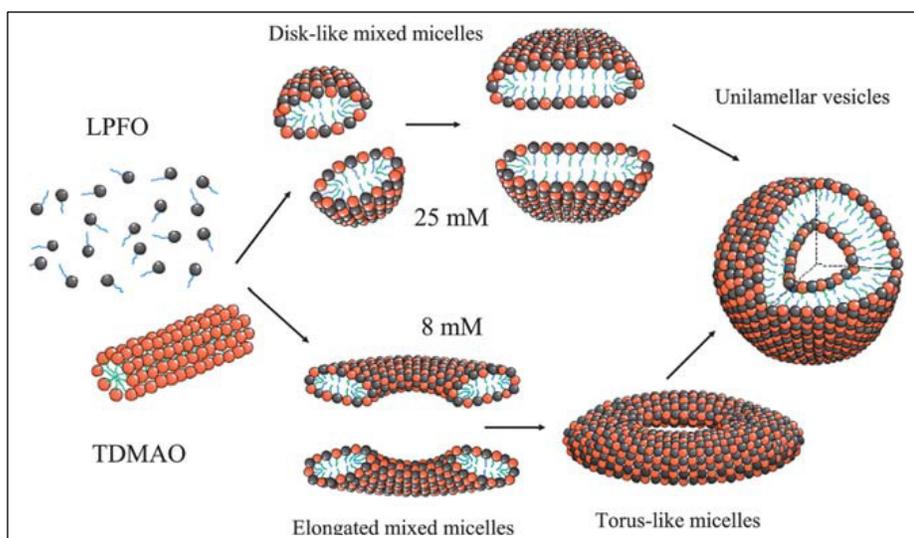


*Figure 8.10 Schematic representation of the two different pathways followed in the formation of ULVs near 25 mM and well below 8 mM, the cmc of the anionic micelles (LPFO), Courtesy Theyencheri Narayanan(DOI: 10.1039/C1SM05354J) [50].*

## 8.5  Lateral Stress Relaxation in Lipid Surfactant Monolayers

The dynamics of lipid surfactant monolayers (traditionally called Langmuir-Blodgett monolayers or films) have been studied because of their technological importance and biological relevance. For physical and chemical scientists they provided attractive models for the study of phase transitions, critical phenomena, and nanoscale dynamics [53]. Biologically, surfactants form lipid monolayers that are indispensable in helping us breathe by stabilizing the large air/water interface in the lungs [54]. During the breathing process the surface area of the lungs changes and that generates stress on the surfactant layer covering the interface. If a two-dimensional surfactant layer is compressed to its stability limit, it explores the third dimension via collapse. Understanding this 2-D-to-3-D transition is of great importance as it provides insight into the origin of defects in thin films [55]. The mode of collapse can be tuned by varying the mechanical properties of the film. In their classic paper, Pocivavsek et al. [56] compare this phenomenon to crumpling a piece of paper. The result is a meshwork of highly deformed ridges and perfectly straight planes appear. The initial response of a compressed membrane resting on water or a gel is wrinkling, producing beautiful sinusoidal undulations across the entire surface. On further lateral compression of the membrane, the wrinkles vanish except for a few folds similar to the geometry on a crumpled paper (see Box 2). In Fig. 8.11, optical images of this phenomena are shown for a 10μm polyester film placed on a water surface (A) and on a gel surface (B), and a 15-nm Langmuir trilayer of colloidal gold film on a water surface (C).



*Figure 8.11  Optical images demonstrating the folding phenomena under compression in (A) a 10 μm polyester film placed on water, (B) the same film over gel, and (C) a 15-nm Langmuir gold film on a water surface (from Ref. 56).*

Various images depict the details of the evolving structure with increased lateral compression. The final increase in compressi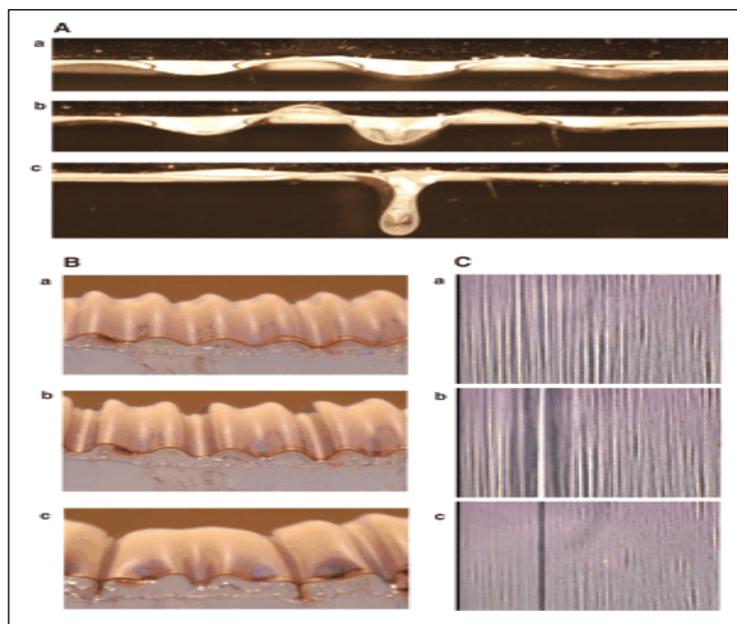on removes the wrinkles and creates local folds. Does one understand the microscopic and mesoscopic origin of the dynamic response and stability of the surfactant layer to compression? The workshop participants focused on this topic, inquiring how x-ray tools could provide new information on the stress relaxation, in-plane rigidity and collapse of lipid monolayers.

A Langmuir monolayer of dodecanethiol-ligated gold nanoparticles suspended in heptane was selected for *in situ* optical microscopy and x-ray scattering studies as a prototypical 2-D system under compression to demonstrate the evolution of the surface behavior over micro- and mesoscopic-length scales [57]. In this study, optical microscopy provided valuable qualitative information about mesoscopic phases and phase transitions. Grazing incidence x-ray scattering provided information about packing symmetry. The initial films contained large islands of particles, which at microscopic level showed voids. structural arrangement will reduce both the film's resistance to shear and the coupling between layers, allowing the layers to bend. Further increases in lateral compression produced wrinkles consisting of multilayers of particles, and eventually the V folds described in Fig. 8.11. Under compression, the film exhibited transition among three phases: monolayer, hash, and multilayer, with wrinkles (and, eventually, folds) developing in the multilayer phase upon further compression.X-ray reflectivity measurements supported the idea that these macroscopic islands consist of many randomly oriented, crystalline domains.

Similar measurements have been performed on self-assembed Ag nanoparticle (NP) Langmuir films at the air-liquid interface utilizing grazing incidence x-ray scattering [58]. The measurements clearly showed ordered periodic wrinkles (perpendicular to the direction of compression) and large-scale folds. Figure 8.12 shows the measured in-plane structure of 2-D crystalline ordering at high lateral compression in Ag and Au nanoparticle films.

The x-ray scattering patterns from the monolayer of Ag nanoparticles do not show any higher order diffraction peaks, while that from the monolayer of the Au nanoparticles display diffraction peaks up to the fourth order representing hexagonal 2-D crystalline order. The authors [58] associate the difference to the amorphous structure of the Ag films due to polydispersity, while the Au nanopartcicle films are highly monodispersive. In addition, the Au nanopartcles form a trilayer structure while a bilayer is observed in the Ag films. This wrinkle-to-folding transition in Au nanoparticle films implies the presence of nonlinear geometric term in the elastic energy of the system, resulting in a scaling relation between the fold subducted length and the wrinkle wavelength. While this scaling has been verified from macroscopic optical images, its validity for systems at the nanometer scale requires further x-ray imaging studies. Studies of the dynamics of monolayer wrinkling and folding in the above prototypical cases could offer important insights into the collapse and folding of biological membranes and cellular structures.

## Box 2: Complexity of Crumpled Papers, Sheets, and Layers

*"A crumpled sheet resembles a cubist's vision of a mountain range: it's a mass of conical peaks connected by a tangle of ridge lines. The peaks and ridges store energy, and as the wad is compressed, their numbers increase so that the total energy contained in the wad grows rapidly. Soon, it requires a tremendous squeeze to supply enough energy to make the wad even a tiny bit smaller............"* Adrian Cho, Phys. Rev. Focus 9, 7 (2002): Comments on **"Crumpling a Thin Sheet",** *Kittiwit Matan, Rachel B. Williams, Thomas A. Witten, and Sidney R. Nagel, Phys. Rev. Lett. 88, 076101 (2002)*

*".......when a flat plane is subjected to distortional stress but only permitted to bend, not stretch, it transforms suddenly and unpredictably into a landscape of folds and facets, each representing an entirely new surface. It's what researchers call a "far from equilibrium" process, guided by strange rules and non-linear effects.....," Brandon Keim, Wired Science, August 22, 2011: Comments on X-ray Tomography research "Three-dimensional structure of a sheet crumpled into a ball", Anne Dominique Cambou and Narayanan Menon, Proc. Nat. Acad. Science 108, 14741-14745 (2011)*
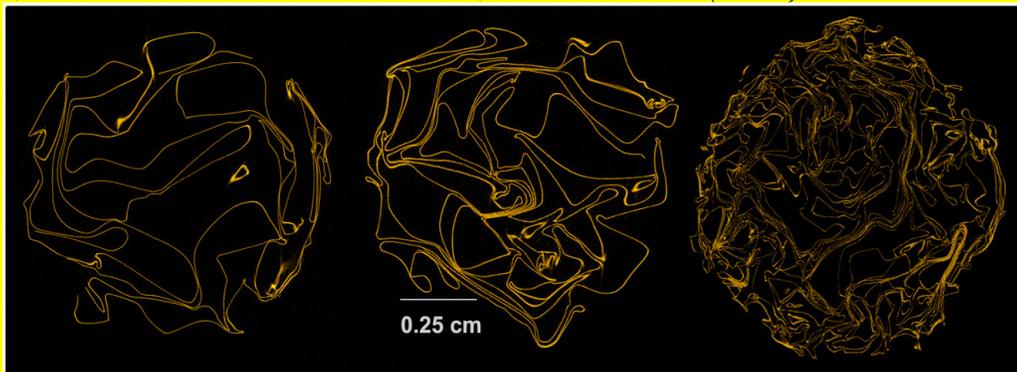


*Reconstructed slices from x-ray tomography images of crumpled spheres of aluminum sheet. The images show slices through equatorial plane of three crumpled spheres with average volume fractions of about 6%, 8.5% and 22%.*

*"......Whether in the buckles of a flower or leaf, the folds of crumpled paper, or the crack tips in a popping balloon, thin sheets naturally develop singularities. In the regions around the singularities, detailed features of the material become important. .......We do not fully understand how that is possible. Many unsolved problems thus stem from the interaction of small and large features of surfaces. Geometry and other large mathematical ideas are not enough to solve those problems; they must have help from the underlying physics." Michael Marder, Robert D. Deegan, and Eran Sharon, Physics Today 60, 33 (2007)*
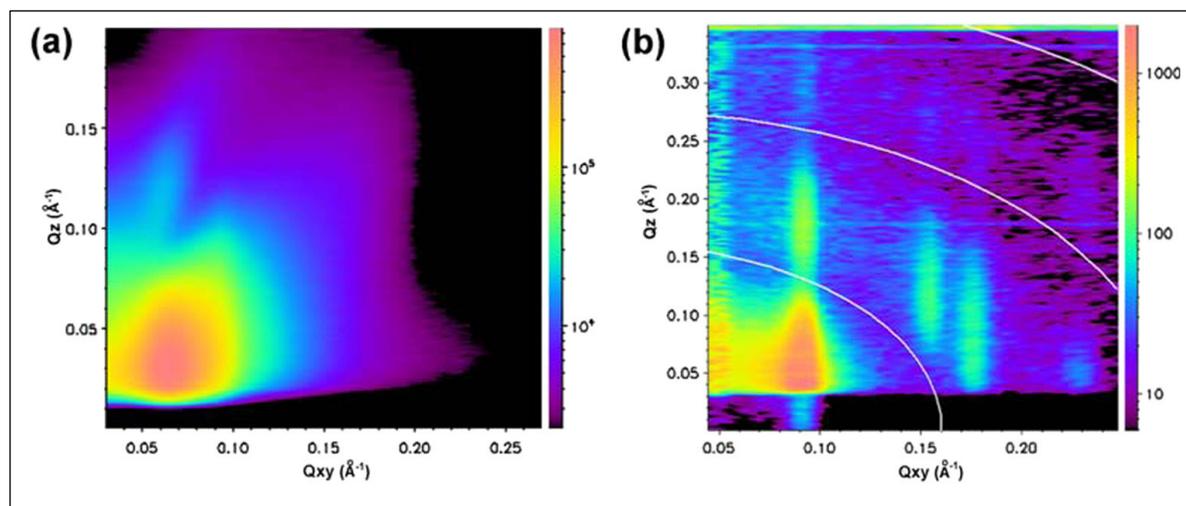
*Figure 8.12  Grazing incidence x-ray diffraction patterns from monolayers of (a) Ag-NPs (at a lateral pressure of 2.7 mN/m), and (b) Au-NPs (at a lateral pressure of 5 mN/m) (from Ref. 58).*

## 8.6  Future Outlook

This workshop focus panel has addressed key areas of complex soft matter and fluids. This topic provides a broad umbrella under which one can fit many far-from-equilibrium research areas covered in this section. Much of the discussed research has direct application in energy (liquid fuel cells, conducting lubricants, electrolytes for lithium metal batteries, fuel ignition, nanoparticle fluids for carbon capture, and nanomaterials for biomass conversion), transport processes in living systems (understanding lung mechanics, tumors, artificial trees, and bioseparations), microfluidics (microscale fuel cells, separation devices, microscale mixing), adhesion (liquid bridges and capillary wetting), and self-assembly. It has been demonstrated that x-ray tools will be a major resource for a fundamental understanding of the evolution and control of complexity in soft matter. Future research challenges can only be addressed through analytical theory, numerical simulation, and experiments that span length scales from picometers to nanometers to micrometers, and from the femtosecond to microsecond time domains. The drive toward developing processes at the nanoscale generates many further challenges. As we have already seen, scaling down exaggerates the importance of interfacial forces and inspires studies of a rich set of transport and adhesion processes that would involve surface-induced chaotic flows for enhancing transport and mixing at the nano- and microscales. There is a new interest in active and responsive soft materials because of their potential use in microactuation systems, sensors, microfluidics, biomedicine, tissue engineering, biomimetics, robotics, and photonics [59, 60]. To fully impact the development of these new interests, it is necessary to develop a fundamental understanding of phase behavior, hydrodynamics, and rheology at the molecular- to microscale-levels as the system responds to external energy increments (through changes in pH, temperature, humidity, electric fields, etc.). The x-ray spectroscopic and scattering techniques available at third-generation synchrotron sources and XFELs would provide the required knowledge.

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# 9  Focus Panel: Nonlinear X-ray Science, X-ray Quantum Optics, and Extreme Metrology

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## 9.1 Introduction and Overview

While nonlinear optics and quantum optics are well established in the regime of visible light, they are largely unexplored at x-ray energies. In this wavelength regime, nonlinear and quantum optics meet the structural granularity of condensed matter, so that these disciplines become sensitive to the details of atomic arrangements and their temporal fluctuations. Thus, one expects conceptually new views into the dynamics of complex systems by translating nonlinear and quantum-optical techniques into the regime of hard x-rays. In contrast to the optical regime, the momentum transfer imposed by x-rays allows one to sample the full reciprocal space that is required to probe non-equilibrium dynamics over all relevant length scales. Simultaneous access to time and length scales of collective structural rearrangements will be possible via coherent spectroscopy at x-ray wavelengths. Due to the high photon degeneracy at x-ray laser sources, nonlinear effects will dominate and cannot be neglected as they are for synchrotron radiation sources. These effects will critically impact all conventional x-ray spectroscopies and form the basis for new experimental techniques. Due to qualitatively different interaction mechanisms, nonlinear techniques that are established in the optical regime cannot simply be transferred into the domain of hard x-rays. The key challenge in this field is thus the understanding of x-ray scattering processes in the presence of high photon degeneracies that form the basis for the emerging disciplines of nonlinear x-ray science and x-ray quantum optics. It is to be expected that fundamental key scientific questions can be successfully tackled in a qualitatively new fashion: What is the intrinsic relation between time and length scales when a system evolves through non-equilibrium states? What role does quantum mechanical entanglement between different parts of the system play in chemical and biological processes?

Nonlinear effects arise when the optical properties of the medium are modified due to the presence of photons. The key quantity that determines these effects is the photon degeneracy, i.e., the number of photons per mode of the radiation field. This number can assume values of $10^9$ for gas lasers and up to $10^{14}$ for mode-locked or Q-switched lasers. At such high photon numbers the light of frequency modulates the microscopic charge distribution, leading to phenomena such as high-harmonic generation, frequency mixing, up- and down-conversion, and more.

The advent of new radiation sources, especially FELs, opens the field of nonlinear optics at x-ray energies. While the photon degeneracy barely reaches 0.1 at existing third-generation synchrotron sources, it will go beyond $10^9$ at x-ray laser sources (see Fig. 9.1). In combination with the outstanding time resolution of these laser sources, x-ray nonlinear spectroscopies might be applied to monitor fast transient processes and intermediate states that are encountered in environments not accessible to optical radiation. Examples are phase change dynamics in correlated electron materials or dynamical processes in tribological systems such as bond formation and bond breaking between two interfaces in frictional contact.
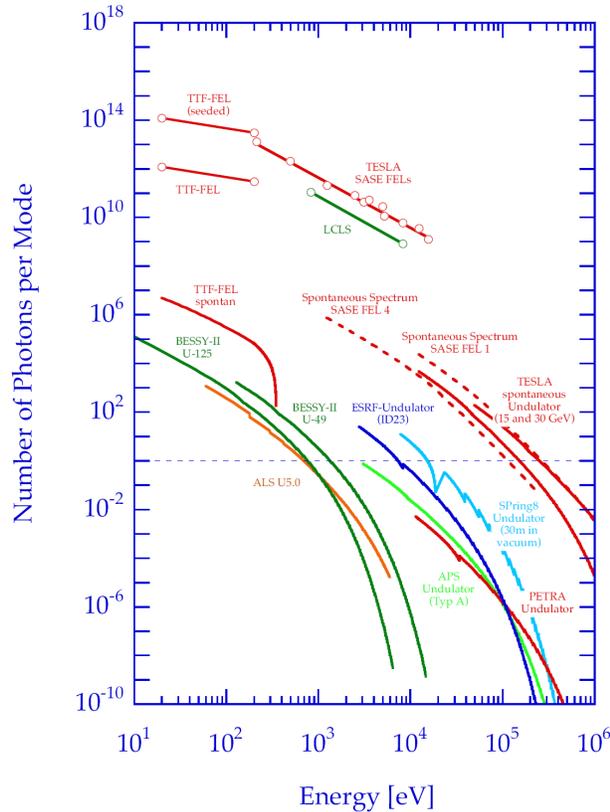
*Figure 9.1  Number of photons per mode for various synchrotron radiation and FEL sources. The horizontal dashed line marks the value N = 1, above which nonlinear effects become relevant. (Figure taken from Ref. 1)*

It should be noted that there are a few nonlinear effects that do not rely on multiple incident photons but rather on vacuum fluctuations, which can have a strong influence due to the high density of electromagnetic modes at x-ray energies. Therefore some effects can be observed even without an FEL. The most prominent of these effects is parametric down conversion (PDC). This process leads to the emission of a pair of photons in an entangled state, i.e., a state that cannot be written as a simple product of photon state and field mode. While PDC has been demonstrated at x-ray energies [2, 3, 4], entanglement of photons at x-ray energies remains to be observed [5]. Possible applications of these entangled states are in fundamental tests of quantum theory and in novel types of spectroscopy. Fundamental studies would include the nonlocality of quantum mechanics via Bell's theorem. Such applications would make use of the high fidelity of x-ray photon detection to close so-called loopholes, but the challenge is lossless transport of the x-ray photons through optics from the source to the detectors. A rather straightforward application is to use the correlation of down-converted photons to in heralded-photon applications (a technical term known from visible-light PDC): One photon in a down-converted pair is used as a reference to indicate with certainty the presence of another on the sample. This permits a drastic reduction of radiation exposure because of the elimination of Poisson statistics normally present in the determination of the incident intensity [6, 7]. Another spectroscopic application making full use of the entanglement property would be two-photon absorption with a linear

dependence on the incident flux of photon pairs (biphotons). This has been predicted theoretically [8, 9] and demonstrated experimentally in the visible wavelength range [10]. Another effect that depends on vacuum fluctuations is the Casimir force. It would be very interesting to extend measurements on the quantum vacuum itself from the microns to nanometers length scales [11].

A central paradigm in the field of quantum optics is the two-level atom. In the optical regime the sharpest atomic resonances are realized in ultracold quantum gases. In the x-ray regime extremely narrow linewidths are observed for nuclear resonances. The hyperfine interaction of these two-level systems with their environment can be rather well controlled and almost the natural linewidth is observed in solid state samples. Resonant (Mössbauer) nuclei can be employed to probe fundamental quantum optical effects such as single-photon superradiance and the collective Lamb shift [12], as has been recently demonstrated [13]. These effects result from the interaction of a large number of identical atoms with a common resonant radiation field. Cooperative effects at x-ray energies have so far been explored in the single-photon regime. It thus appears to be very appealing to investigate such effects in the multi-photon regime.

The interaction of many identical resonant atoms with a radiation field plays an important role for fast radiative energy transfer as it occurs in light-harvesting systems in photobiology. Systems of identical resonant atoms can thus serve as a model system to explore these effects in a systematic fashion, as they are crucially dependent on the geometric arrangement of the resonant atoms.

Nonlinear optics, however, is not the domain of only extremely high photon numbers. Nonlinear optics at low photon numbers require materials with optical properties that are significantly altered even by single photons. When this alteration persists long enough to be experienced by photons that subsequently interact with the material, large nonlinearities can be expected. Nuclear resonances with lifetimes in the range between picoseconds and nanoseconds are interesting candidates in this field. Alternatively, nonlinear optical effects at low light levels can be reached with resonant atoms placed in a high-finesse, small-volume cavity. Yet to be explored are the conditions at which this can be achieved at the energies of hard x-rays.

Recently, laser-based spectroscopy opened unique possibilities for ultrahigh-precision measurements of physical quantities by application of the frequency comb technique [14]. One aim of this focus panel was to explore how these concepts can be pushed to shorter and shorter wavelengths. The ultimate goal would be the increase of the precision of the frequency comb technique into a regime where one could probe the temporal variation of fundamental physical constants as postulated within certain cosmological models.

An important requisite that is indispensable for future studies outlined above is multicolor x-ray laser radiation with a well-established control of longitudinal coherence (i.e., monochroma-ticity) that can be achieved by seeding [15] or XFEL-oscillator schemes [16]. Under such conditions a precise coherent control of atomic and nuclear transitions becomes possible and forms the basis of nonlinear and quantum-optical effects in the x-ray regime.

## 9.2 Nonlinear Science

Nonlinear optics mainly utilizing visible light (with long wavelengths of 400-760 nm) has been under development for more than 50 years. Progress has been made in the fields of basic and applied research, such as wavelength conversion and ultrahigh-speed optical communication. Nonlinear x-ray science is a new entry in the field of quantum x-ray optics. There is little knowledge about the nonlinear interaction of hard x-rays with matter except the fact that the cross sections are much smaller than those of visible light. In spite of this fact, the potential for this field is vast and can provide great insight into the dynamical couplings between core and valence states, and a new window on electron dynamics. Ultrafast electron dynamics lies at the heart of material response to electromagnetic fields, and so we must identify the *key experiments* that will provide a far more complete picture of the interaction of large complex quantum systems and x-rays. Understanding ultrafast electron dynamics underpins the next generations of technology.

Nonlinear optics will play an increasing role in the way that x-ray light sources are being used. Most experiments on current synchrotron light sources can be understood without ever considering nonlinear-optical effects, but the much higher degree of photon degeneracy of next-generation sources, especially XFELs, will make them prevalent. Proper interpretation of data will require the inclusion of nonlinear-optical effects, and novel techniques can be devised with them.

In the hard x-ray regime, the radiation wavelength is smaller than or comparable to the characteristic atomic separation in the condensed system, and hence the response of a crystal to the field is extremely sensitive to the microscopic structure. This leads to the influence of crystal symmetry on the observed non-linear response. For example, the local response depends on the coordinates of atoms in the lattice, and therefore the medium no longer can be considered as homogeneous. Second-order nonlinearities can be observed from free electrons (weakly bound compared to the x-ray photon energy) because the Lorentz-force type interaction is intrinsically non-centrosymmetric.

### 9.2.1 Nonlinear X-ray Spectroscopies

At the high degeneracy parameter values relevant to an XFEL, stimulated inelastic (Raman) x-ray scattering will overwhelmingly dominate over the photon-hungry, spontaneous process used in synchrotron-based RIXS.

An interesting scenario arises if the sample is illuminated by two laser beams, the frequency difference of which corresponds to the frequency of an excitation within the system. In this case, stimulated emission at the difference frequency is observed (stimulated Raman scattering) that allows for an extremely high sensitivity in probing excitations in molecular systems or the identification of species' particular vibrational modes that form transiently during a sequence of non-equilibrium processes. It appears to be extremely intriguing to extend these concepts into the x-ray regime [17].

If radiation damage is not excessive, stimulated Raman scattering can be utilized to efficiently pump selected excitations, in bulk, with chemical specificity and independent of dipole selection rules. After

coherent evolution, these can then be sampled utilizing the x-ray analog of t-CARS (time-resolved coherent anti-Stokes Raman scattering) or TGS (transient-grating spectroscopy), as illustrated in Fig. 9.2.

t-CARS is an established method in optical spectroscopy [18]. A stimulated Raman scattering ($\omega_1$, $\omega_2$), or alternatively, a sufficiently short impulsive stimulation is utilized to prepare a coherent superposition of low-lying excited states $f$, and after a time delay $\tau$, this superposition is queried by a second $\omega_1$ pulse, which produces the homodyne-detected anti-Stokes signal $\omega_s$. Since the superposition of states $f$ will evolve during the delay, quantum-beats at the $f$-state splitting $\delta\Omega$ will be detected as $\tau$ is varied. This is the basis of the coherent x-ray scattering method proposed by Tanaka and Mukamel [19].
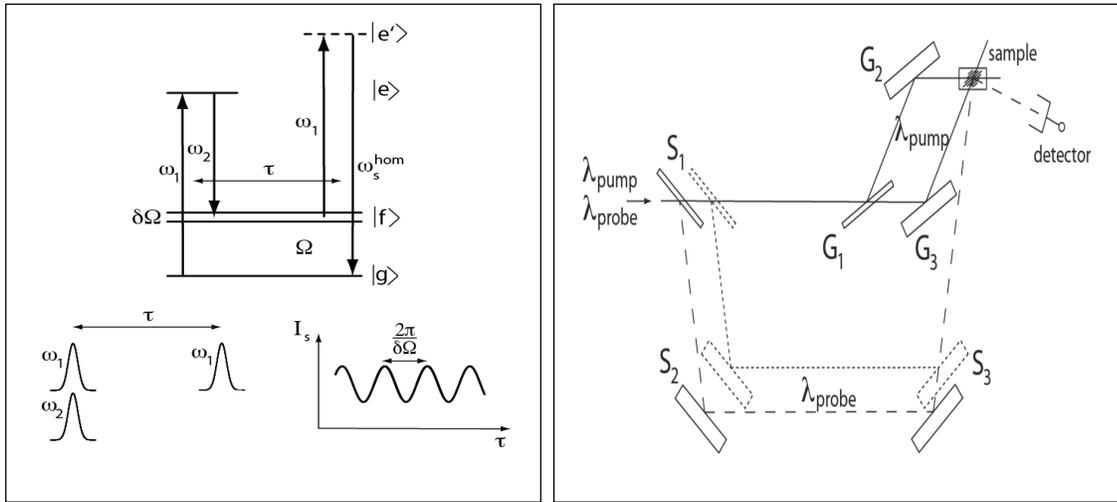


Figure 9.2  Left: The time-resolved coherent anti-Stokes Raman scattering (t-CARS) technique. Right: Diffraction-based geometry for transient grating spectroscopy, Couresy B. D. Patterson [17].

Transient grating spectroscopy [20, 21] is an elegant method of detection for transient optical effects, which allows direct control over the wave-vector $q$ of the excitation and spatial discrimination of the signal wave. The principle of TGS is that a pump pulse is split and the two halves are recombined at the sample under a relative angle $\theta$, to produce a standing wave of periodicity $D = 2\pi/q = \lambda_{pump}/2\sin\theta$ (Fig. 9.2). Interaction of the standing wave with the sample generates an oscillating, spatially-periodic distribution of excitation in the form of a transient grating, which survives for the lifetime of the excitation. A delayed probe pulse is then diffracted by the grating and measures its strength after a delay $\tau$.

Efficient use of such stimulated x-ray scattering techniques will require two-color x-ray pulses, at tunable soft [22] or hard wavelengths [23], with photon energy separation dE = 0.2 - 2 eV and a variable delay dt = 0 - 2 ns.

### 9.2.2  Parametric Down-Conversion

Much of nonlinear optics research is dedicated to the effect of parametric down-conversion (PDC) and its applications in quantum information and communication science. During PDC, a pump photon with

energy $E_p$ from an intense laser passes through a nonlinear medium and decays into two photons: a signal photon with $E_s$ and an idler photon with energy $E_i$.

This effect of a photon decaying spontaneously into a pair of highly correlated and even entangled photons in a nonlinear optical medium can be understood as four-wave mixing driven by vacuum fluctuations. The converter medium is a crystal of some light element, such as diamond. Because the binding energies of the constituent electrons are much lower than hard x-ray photon energies, the approximation of free electrons undergoing transverse oscillations under the influence of the electric field of one wave is applicable.

The magnetic field of another wave can then induce longitudinal oscillations through the Lorentz force, which can emit into the directions of other, diffractively coupled waves - hence the need for a crystal.
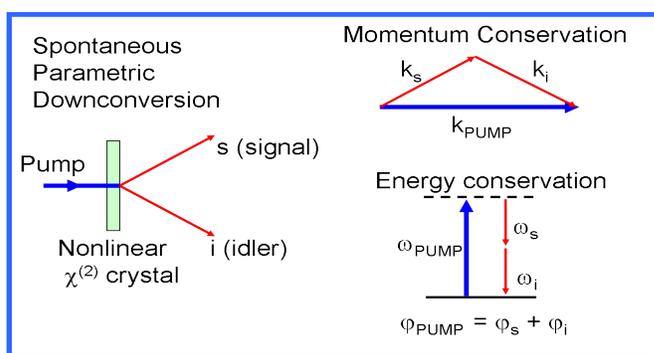


*Figure 9.3  Spontaneous parametric down-conversion (SPDC): A nonlinear crystal splits incoming photons into pairs of photons under conditions of energy and momentum conservation. SPDC is stimulated by random vacuum fluctuations, as such the photon pairs are created at random times. The phase matching dictates the photon pair to be entangled in the frequency domain: If one photon of the pair (the signal) is detected at any time then we know its partner (the idler) is present.*

This extremely weak nonlinear response is somewhat offset by the high modal density at x-ray photon energies, i.e., strong vacuum fluctuations driving the process. Even so, XPDC (Figs. 9.3-9.4) is a weak effect, and the highest event rate observed to date is about 0.1 per sec at an incident x-ray flux of $10^{12}$ per sec [24].

Parametric down conversion could be applied to combine the spectral information delivered by resonant soft x-ray diffraction with the atomic resolution provided by diffraction of hard x-rays. While soft x-ray resonant diffraction is a powerful tool to study 3*d* metal compounds, such as strongly correlated materials, its spatial resolution is limited by the wavelength. Parametric down-conversion of x-rays into soft x-rays (see Fig. 4) can realize angstrom resolution, because the spatial resolution is determined by the pump x-rays while the resonance property is sensed by the soft x-ray idler [25].

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*Figure 9.4  Parametric down-conversion of hard x-rays involving a soft x-ray idler. This approach allows one to combine soft x-ray spectral information with atomic resolution provided by the hard x-ray pump photons, Courtesy K. Tamasaku [25].*



*Figure 9.5  Crossover from linear to quadratic intensity dependence in two-photon absorption utilizing entangled photons [10].*

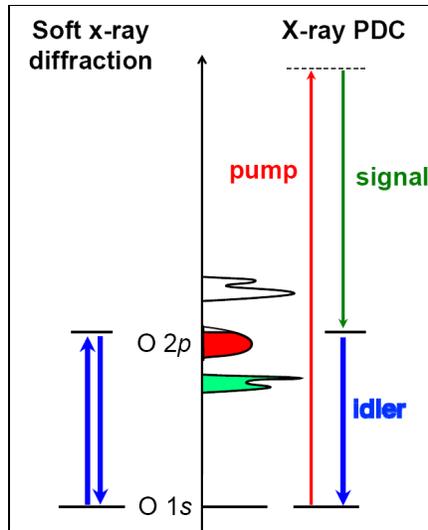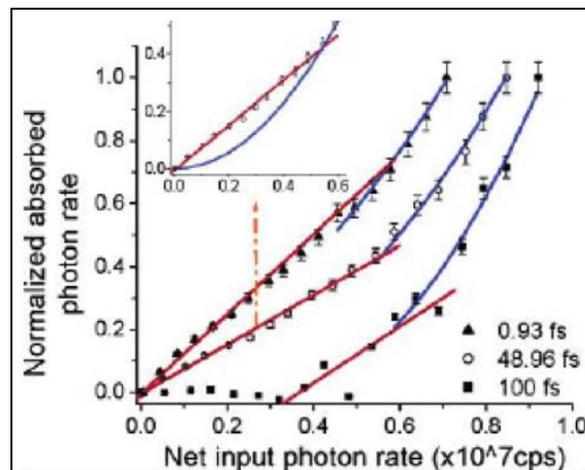PDC can be employed in interesting applications and gives a glimpse of how subtle quantum effects can be used in experiments. An example is the possibility of utilizing entangled photons from down conversion to do two-photon spectroscopy with linear intensity dependence, instead of quadratic as one would normally expect in two-photon spectroscopy. This has been demonstrated with near-visible light (see Fig. 9.5), and a demonstration with x-rays appears to be quite feasible.

It is as if the entangled photons remember that they originated from one. Even though the two photons originated from one, they can be manipulated independently, thus making spectroscopic features accessible that are forbidden in single-photon interactions without exposing the sample to high radiation levels. This is especially important with biological samples. A conceptually even simpler application of XPDC would be a drastic reduction of radiation exposure of biological samples due to sub-Poisson statistics made possible by utilizing one photon of the down-converted pair as a reference indicating the other incident on the sample (heralded photon) [7].

To obtain a significant efficiency in generating entangled pairs of x-ray photons or even multiphoton entangled states, one might adopt a scheme that was recently applied in the UV regime of the spectrum [26] (see Fig. 9.6). The key idea in this study is to place an SPDC nonlinear crystal inside a passive optical cavity designed to dramatically enhance the power of the UV femtosecond laser pulses needed for the down-conversion process. A resonant pulse train coherently builds up inside the femtosecond enhancement cavity, resulting in a significantly higher intracavity power than that available from the incident pulse train alone. This scheme resembles quite closely that of an XFELO, sketched in Fig. 9.11.
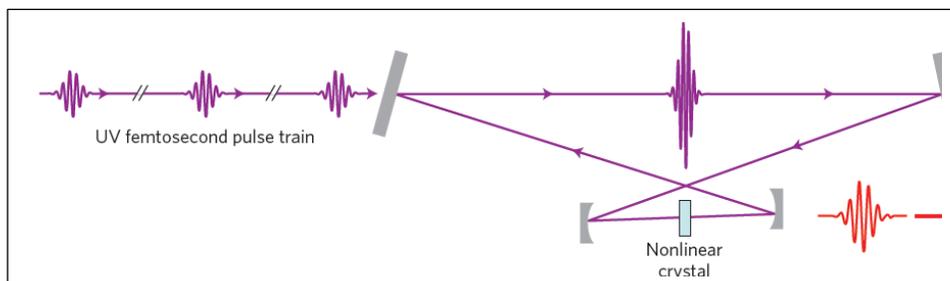


*Figure 9.6  UV femtosecond enhancement cavity for intracavity spontaneous parametric down conversion [26, 27], resembling closely the layout of an XFELO.*

Further key challenges for non-linear x-ray optics are to identify materials that can be used without damage for nonlinear science at future radiation sources. These will most likely have high-efficiency, non-linear effects, allowing the use of lower incident fluxes and material properties such as high x-ray transmittance, high damage-threshold, and high thermal conductivity.

## 9.3 Entanglement, Quantum Control and Cooperative Emission

### 9.3.1 Can We Establish Quantum Optical Control Techniques in the Hard X-ray Regime?

Initiated by the invention of the laser, the field of quantum optics has been a remarkable success story, which has led to the possibility of controlling the dynamics of a variety of quantum systems, in many cases almost at will, giving rise to a broad range of applications. Usually, the development of coherent control methods evolved from being a research subject itself to an enabling technique for further work. Starting from initial proof-of-principle experiments, a similar self-stimulating progress can be expected in the hard x-ray frequency range as well. While a number of techniques can be taken over from the visible frequency range, the unique properties of light-matter interaction at the x-ray frequency range require fresh ideas and second thought.

The least demanding approaches in terms of the light source are related to the coherent control of cooperative emission in nuclear resonance scattering. In a typical experiment, an incident synchrotron radiation pulse hits a solid state target enriched with Mössbauer nuclei, exciting at most one out of a large number of nuclei in the target. Since in coherent forward scattering it is unknown which nucleus is excited, the intermediate scattering state has an excitonic nature, which in turn gives rise to a rich cooperative dynamics. In a groundbreaking experiment [28], it was shown that a sudden rotation of a magnetic field applied to the nuclei can be used to cancel the cooperative decay and restart it at a later time. This switching relies on quantum mechanical pathway interference, and is in direct analogy to one of the most successful techniques in atomic quantum topics, electromagnetically induced transparency [29]. Recently, it was shown theoretically that more advanced coherent control schemes based on this technique enable one to generate entangled light in the hard x-ray regime [5] (see Section 9.3.3, below).

It should be mentioned that a number of fascinating effects have been predicted theoretically based on the cooperative decay of suitably prepared initial states of the ensemble. A recent experiment successfully demonstrated the generation of the required initial, purely superradiant state in an optically thick sample and verified one of these predictions [10], the cooperative Lamb shift [12]. Efficient state preparation and coherent control would open the door to exploring other predictions related to cooperative emission.

A first key experiment would be an advanced implementation of the coherent control techniques in $^{57}$Fe [28], with a versatile control over the applied magnetic field. Since present-day facilities satisfy the demands of such an experiment, this important first step could be taken in a short time frame. Based on this key element, the next steps would be the generation of x-ray entanglement (see Section 9.3.3), direct phase imprinting on the intermediate cooperative exciton state, or the study of quantum mechanical transport processes (see Section 9.3.5).

A related, but much more demanding approach to coherent control of nuclei is the direct driving of nuclear transitions with FEL radiation [30]. This not only involves a sufficiently high photon mode degeneracy in order to actually have a strong enough coupling between the x-rays and the nuclei, but from the point of view of coherent control also requires, at best, full longitudinal coherence of the FEL radiation. The fundamental difference between incoherent and coherent driving can already be seen

from the fact that incoherent driving cannot lead to a population inversion on a directly driven transition, for which the Rabi oscillation undergone by a coherently driven transition allows to achieve inversion. More advanced coherent control schemes in this area would require FEL beams with two or more colors, ideally not only longitudinally coherent by themselves, but also phase locked with respect to each other.

### 9.3.2 Coherent Control of Nuclear Excitations

Coherent control of nuclear excitations would be a powerful tool for preparation and detection in nuclear physics, with applications, e.g., for the release of energy stored in long-lived nuclear excited states.

Two possible scenarios of coherent population control of nuclei have been discussed. The first one involves two-color coherent XFEL light that drives two nuclear transitions in a three-level system, such as the one presented in Fig. 9.7 [31]. Stimulated Raman adiabatic transfer between the two ground states is to be investigated. To bridge the gap between photon and nuclear transition energies, which are above the energy limits of present x-ray coherent sources, it was proposed to use accelerated target nuclei. The Doppler shift brings nuclear transition and photon energies in resonance and also offers an alternative for stimulated Raman adiabatic passage (STIRAP) utilizing a single-color source. For this scenario, it was found that the intensities required for complete coherent population transfer are approaching the designed parameters of the seeded XFEL and the XFELO. The main experimental issues here are that at present, x-ray coherent light sources are not available at the few large ion acceleration facilities, and table-top solutions do not offer the required beam resolution and focusing.

The second scenario is based on cooperative effects in nuclear forward scattering of synchrotron radiation on a nuclear three-level system [31]. As before, the nuclei initially are in state 1, and the goal is to transfer the nuclei to state 2 by applying a single x-ray pulse between 1 and an intermediate excited state 3, followed by spontaneous emission to 2 (see level scheme in Fig. 6). In single nuclei, the final state populations and the pumping performance would be governed by the constant branching ratio of the excited state populated by the x-ray pulse. However, in ensembles of nuclei, cooperative excitation and decay leads to a greatly modified nuclear dynamics, which has to be characterized by a time-dependent cooperative branching ratio. Since the coherent cooperative decay of the nuclei can be controlled, e.g., by changing the direction of the hyperfine field in a magnetic host material [28] or by imprinting phase patterns on the excited nuclear ensemble. This way, one can steer the nuclear x-ray pumping and nuclear dynamics in nuclear forward scattering NFS involving a nuclear three-level system in which only one of the transitions is driven by x-ray radiation. For realistic nuclear forward scattering (NFS) parameters, the control efficiency is limited not by the intensity of light (as in the case of nuclear STIRAP) but rather by the short time range of the coherent decay, i.e., by the nuclear exciton properties. Requirements for coherent control of nuclei in this setup are thus not related to the light source properties but on a superradiant nuclear decay in the sample [31].

### 9.3.3 Can We Bring Non-Classical Photon Science to the X-ray Range?

Non-classical photon science, and in particular entanglement, are highly desirable goals for a number of reasons. On an abstract level, a successful demonstration of the generation of entanglement by means of coherent control followed by a verification of the entanglement would be a remarkable proof of control over the quantum dynamics of nuclei as it is required for most more advanced coherent techniques.

This could trigger the self-stimulating technological progress mentioned before. But entanglement itself is also of interest. Since x-ray photons can be detected with near-full efficiency, an entanglement test in the hard x-ray regime not only advances entanglement research into a new parameter regime based on nuclei being a rather complex model system, but also could lead to a violation free of detection loopholes. This would form an important contribution to the foundations of quantum mechanics.

Next, quantum-assisted measurement schemes based on entanglement could allow for an improved sensitivity, potentially with much weaker light beams. Obtaining sufficient measurement resolution with less-extreme light conditions has potential applications in destruction-free measurements, e.g., of biological samples (see below). An alternative to entangled states of light are squeezed states, which can be used to achieve measurement uncertainties below the standard quantum limit. Finding ways of combining such low noise measurements with the precision associated to the short wavelength of hard x-ray radiation can be expected to lead to significant impact on optical measurement and structuring techniques.
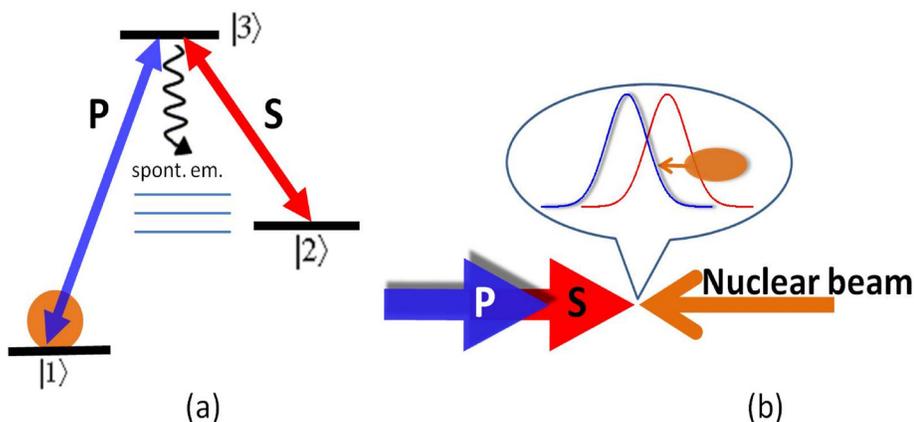


*Figure 9.7  Level scheme for coherent control of nuclear excitations. The initial nuclear population is concentrated in state 1.  The upper state 3 decays also to other states through spontaneous emission. (b) Two partially overlapping and co-propagating x-ray laser pulses P (pump) and S (Stokes) interact with relativistically accelerated nuclei. The Doppler Effect ensures that both nuclear transitions are in one-photon resonance with the laser pulses.*

A key experiment is the generation of entanglement utilizing coherent control of cooperative decay in nuclear forward scattering. For this, the coherent scattering of the synchrotron radiation pump pulse can be  controlled by a sequence of magnetic field switchings such that two coherent decay pulses with different photon polarizations are emitted ([4], see Fig. 9.8). Depending on the switching sequence, the

two pulses can be emitted as either time-resolved or overlapping in time. Since the synchrotron radiation pulse typically creates only at most one (and more often no) nuclear resonant excitation in the target, only one photon will be emitted in either of the two field modes, with no way of knowing in which one. This lack of knowledge leads to the entanglement of the two modes. In a proof-of-principle experiment, the entangled signal could be separated from the background by utilizing time gating. More advanced setups could apply x-ray polarizers and piezoelectric fast steering mirrors to spatially separate the entangled signal from the background [5].



*Figure 9.8 Prototype setup for entanglement generation via coherent control of cooperative decay in nuclear forward scattering. Incident light is monochromatized and hits the target, in which coherent control techniques are used to split a single excitation into two different polarization modes, which are indicated as the entangled state. The right-hand side is an interferometer setup to verify the nonclassical correlations.*

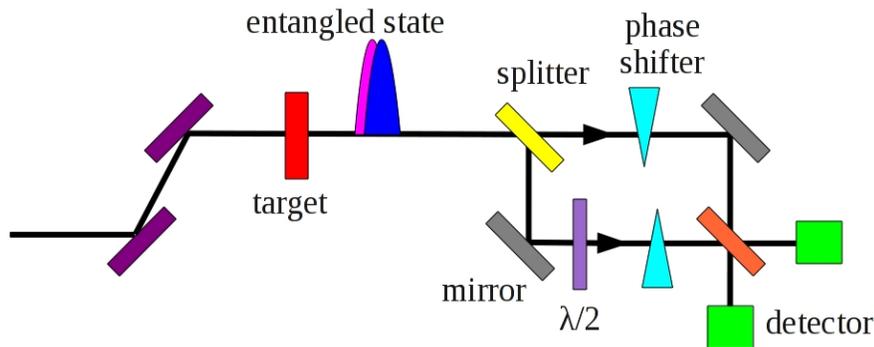This entanglement could be detected utilizing an interferometer setup, with a splitting of the two single-photon entangled modes, followed by a subsequent recombination of the two modes on a beam splitter and correlation measurements on the two beam splitter output ports. By monitoring the correlation signal in dependence on phase shifts applied to the two beams separated in the interferometer, a Bell-type inequality can be violated [32], thereby verifying the entanglement. The most straightforward implementation would rely on background removal by time gating and an input state of temporally overlapping entangled modes with different polarization, such that the two pulses arrive simultaneously at the detectors for the correlation measurement. A different approach to verify the presence of entanglement is to implement a quantum protocol relying on entanglement, such as quantum state teleportation [32]. Experimentally, however, this is more challenging than the violation of Bell inequalities, because in addition to the entangled photon state, the simultaneous presence of a photonic signal state to be teleported and more-advanced correlation measurements are required.

It should be noted that correlation measurement setups as required for the entanglement verification could also be used to measure correlation functions of the light in the sense of Glauber. This is of importance because the usual intensity measurements cannot distinguish classical from quantum light. For this, the measurement of higher-order correlation functions is required. Next to the fundamental importance, such higher order correlation measurements have applications in improved measurement sensitivity, and via the Hanbury-Brown-Twiss effect could be used to characterize the synchrotron light source.

### 9.3.4 Improved Metrology Schemes with Nonclassical States of Light

A key experiment is the demonstration of sub-wavelength precision in an x-ray interferometer based on quantum-mechanical many-body entangled [|N,0><0,N|+ [|0,N><N,0|] states, referred to as NOON states [33]. For this, an entangled photon pair generated in parametric down-conversion can be directed on a beam splitter, which by virtue of the Hong-Ou-Mandel effects [34] leads to the generation of a NOON state of the form (|20> + |02>). Directing the two output ports with the entangled state into the arms of an interferometric setup, the improved resolution could be detected via the dependence of the obtained interference pattern to the phase shift applied to the light in one arm by a material sample. (Key experiment: Determination of pulse length with femtosecond resolution.)

### 9.3.5 Modelling of Quantum Transport Processes: Can We Find Transport Processes that Are Stimulated By Noise?

A more long-term perspective for the application of coherent control and non-classical physics in x-ray science is the experimental exploration of quantum mechanical transport processes. One important motivation for this is given by recent experimental results on the underlying physical mechanisms for biological energy transport processes, such as in photosynthesis [35]. In a simple model, energy is absorbed by a harvesting unit, then sent over a transport channel, and finally arrives in a complex that converts the photon energy into resources for the plant. Remarkably, the transport channel operates with high efficiency and robustness, even though the biological environment is far from perturbation free. This robustness and effectiveness could be due to quantum effects, and recent experiments show that quantum beats can be observed in relevant biological structures at room temperature over sufficiently long time scales [36, 37]. While already a large number of theoretical works are dedicated to modeling, an experimental study of quantum mechanical transport in a controlled environment is challenging. It turns out that nuclear forward scattering of hard x-rays could form an interesting alternative to possible setups in the visible frequency range [39]. A possible setup is shown in Fig. 9.9.
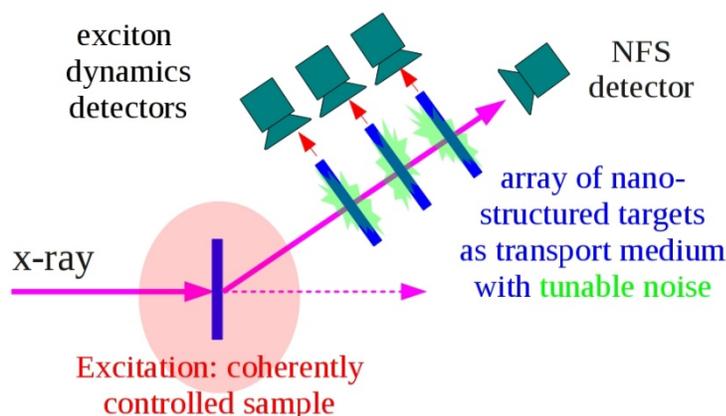


*Figure 9.9  Scheme of a setup to model biological energy transport processes via nuclear forward scattering of hard x-rays, Courtesy J. Evers[38]. An array of nanostructured targets serves as a transport medium with tunable noise to simulate conditions that are relevant in biological processes.*

The x-ray pump hits an initial target, which models the light-harvesting unit. This initial excitation is then directed toward the transport channel, for example, utilizing the nuclear lighthouse effect [12], or coherent control of the forward scattering direction. This procedure allows for a controlled initial excitation without introducing correlation or coherence between the initial excitation and the control channel. While in principle the initial target could be removed such that the x-ray light from the source directly hits the transport channel, the intermediate target allows modeling the relevant biological setups more closely, and nanostructuring the target gives more flexibility in the excitation dynamics through the transport channel. The transport channel is formed by a number of target foils, which are separated by a macroscopic distance. The individual target foils can be varied, e.g., in thickness, line splitting, resonance frequency, or the spatial structure to model different topologies of the transport channel. In addition, the spatial separation of the individual elements of the transport channel allows for an individual addressing of the different foils, e.g., to apply uncorrelated noise to different parts of the channel. This could be achieved, e.g., utilizing magnetic fields, electric fields, laser fields, or vibrations. Such noisy channels are of considerable interest from a fundamental point of view, and are of relevance since biological transport channels are embedded in a noisy environment. Theoretical calculations suggest that noise could in certain situations be beneficial to quantum transport rather than detrimental [39]. The dynamics of the energy transport through the channel can be monitored by placing detectors sensitive to incoherent decay channels next to each target foil, and a detector in the forward direction in order to measure the time-dependent energy transfer to the final site in the transport chain. A major goal of such studies could be the identification of conclusive experimental signatures to verify the presence of quantum effects, which could then be applied to biological transport channels. But also independent of biological applications, the understanding and control of energy and information transport at the microscopic scale in many particle quantum mechanical systems could lead to important applications related to communication or energy science, for instance.

### 9.3.6 Fundamental Aspects of Superradiance and Cooperative Emission

Next to coherent control, the fabrication of nanostructured targets and the embedding of active target layers into suitably tailored nanocavities also form an important requirement for a successful experimental exploration of cooperative decay. Based on these techniques, a recent experiment could realize the excitation of an almost perfectly superradiant state in an effectively thick nuclear target, which cannot be achieved by conventional direct excitation of a thick target with synchrotron radiation [13]. This key advance allowed for verifying experimentally a recently discovered consequence of cooperative decay in extended media, the cooperative Lamb shift [12]. Based on this purely superradiant state in an extended thick sample, a number of fascinating effects have recently been predicted theoretically [40], often resulting in a heated discussion on the interpretation [41]. An experimental exploration of these questions would lead to much better understanding of cooperative emission in extended samples, and at the same time connect x-ray quantum optics to other areas across physics, such as multiple scattering and cooperative emission in cold gases. A further exploration of efficient target nanostructuring and coherent control would open the door to exploring other predictions related to cooperative emission.

## 9.4 Controlling the Longitudinal Coherence

The spectral resolution of any x-ray scattering technique relies on the degree of monochromaticity of the x-ray source. In order to circumvent the stochastic nature of the SASE emission process, several seeding schemes have been proposed that rely on the controlled interaction of the travelling electrons in the undulator with a tailored beam of photons. A very promising self-seeding scheme has recently been proposed that is based on the action of a Bragg reflection as a "wake monochromator" in the baseline of an XFEL [15].

In essence, self-seeding with a wake monochromator consists of a setup formed by the following components:

i.   *A first part of the undulator giving SASE radiation in the linear regime*

ii.  *A weak chicane to be installed within an undulator cell (e.g., 4 m for the LCLS); a momentum compaction of several  microns is enough to*
         *-wash out the electron beam microbunching at 1.5A*
         *-introduce a tunable bunch delay between electrons and photons*
         *-introduce a transverse offset of a few millimeters*

iii.  *A wake monochromator, introduced in the offset created by the chicane*

iv.  *A second undulator part*

Radiation and electrons are separated in the chicane. Radiation goes through the wake monochromator, consisting of a single crystal in Bragg geometry. The forward diffracted beam is considered. Once the orientation of the crystal is fixed, the crystal behaves as a bandstop filter, as illustrated in Fig. 9.10.

The presence of a hole in the spectrum corresponds, in the time domain, to a trailing wake, which can be used for seeding the electron bunch.

The method solves the problem of poor longitudinal coherence for hard x-rays, yielding a relative bandwidth down to $10^{-4}$ for Q=0.025 nC  ($10^{-5}$ for Q=0.25 nC). Moreover, it is of low cost because there is no need for a long electron bypass, but only for a weak chicane. Moreover, there is no need for a special photo-injector setup. The method is robust and risk-free and the baseline mode of operation of the XFEL is not disturbed.
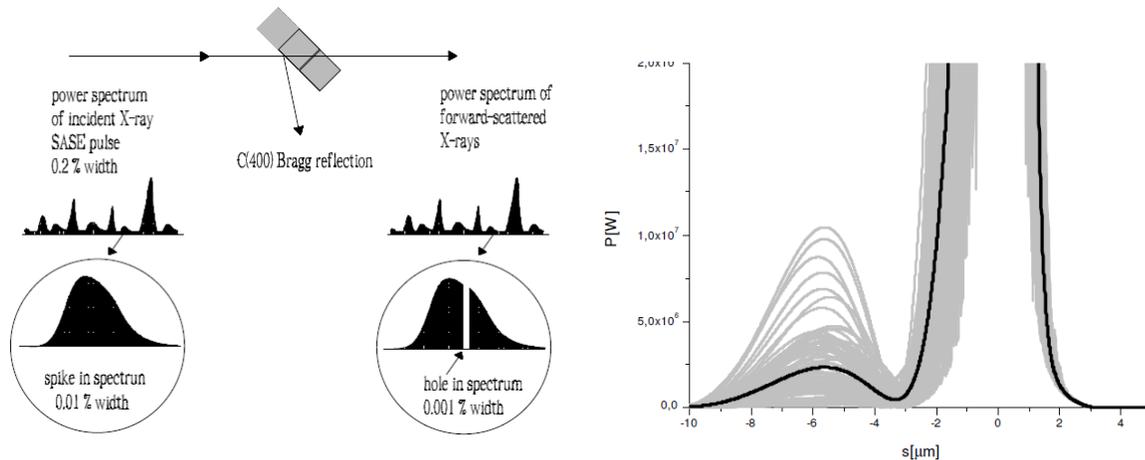
*Figure 9.10  Left: A single crystal in Bragg geometry acts as a bandstop filter for the transmitted x-ray SASE radiation pulse. The transmittance of the crystal shows a narrow-band absorption resonance when the incident x-ray beam satisfies the Bragg diffraction condition. The temporal waveform of the transmitted radiation pulse is characterized by a long monochromatic wake. After the crystal, the monochromatic wake of the radiation pulse is combined with the delayed electron bunch and amplified in the downstream undulator, Courtesy Gianluca Geloni [15].*

## 9.5  Extreme Metrology

Current theories that attempt to unify gravity with the other fundamental forces can lead to spatial and temporal variations in the fundamental constants [42]. Is there a unique opportunity or potential for hard x-ray metrology to perform a laboratory search for the variation in fundamental constants? What kind of source and experiment will provide us with the required accuracy to perform this laboratory experiment in a reasonable measurement time?

### 9.5.1  Frequency Comb

The question of variation in the fundamental constants has been at the center of cosmology research for decades [42]. The development of optical metrology utilizing frequency combs are the best-known approaches in such investigations. Recently, there has been a remarkable synergy between the technologies of precision laser stabilization and mode-locked ultrafast lasers. This has resulted in control of the frequency spectrum produced by mode-locked lasers, which consists of a regular comb of sharp lines. Thus, such a controlled, mode-locked laser is a femtosecond optical frequency comb generator. This involves the use of ultrafast lasers, fiber optics, and optical cavities to create highly correlated light pulses. The pulses have a spectrum that consists of an evenly spaced frequency comb of thousands of sharp spectral lines. A mode-locked laser produces a wide comb of evenly spaced frequency modes in the frequency domain. The frequency comb may be seen as the direct result of a sequence of coherent short pulses in the time domain. The combs also provide a direct bi-directional link between laser and envelope frequencies. For a sufficiently broad comb (octave spanning), it is possible to determine the absolute frequencies of all the comb lines. This ability has revolutionized optical frequency metrology

and synthesis. It has also served as the basis for the recent demonstrations of atomic clocks that utilize an optical frequency transition. In addition, it is having an impact on time-domain applications, including synthesis of a single pulse from two independent lasers.

The accuracy of optical frequency combs has exceeded $10^{-14}$ [14, 43]. This can be further increased by going to shorter-wavelength frequency combs.

A promising method for extending frequency comb spectroscopy to the extreme ultraviolet is high-order harmonic generation of an infrared frequency comb at the focus of a high finesse cavity. A first-generation system was able to achieve greater than 100 nW of average power up to the 21st harmonic at 51 nm [44,45,46].

The cavity enhancement technique could also potentially be used with similar average intracavity power to seed an echo-enabled harmonic-generation FEL [47,48], which requires only modest laser seed energies. In this scheme, electron bunch energy modulation would occur at a short undulator placed at the intracavity focus of the enhancement cavity.

It thus appears to be extremely intriguing to extend this concept way into the x-ray regime. A suitable source could be a mode-locked, high-rep-rate XFEL together with the necessary optics, similar to the concept of the XFEL-oscillator (XFELO) (see Fig. 9.11). It is evident, however, that such a device poses extreme challenges to the stability and phase control of the electron bunches.
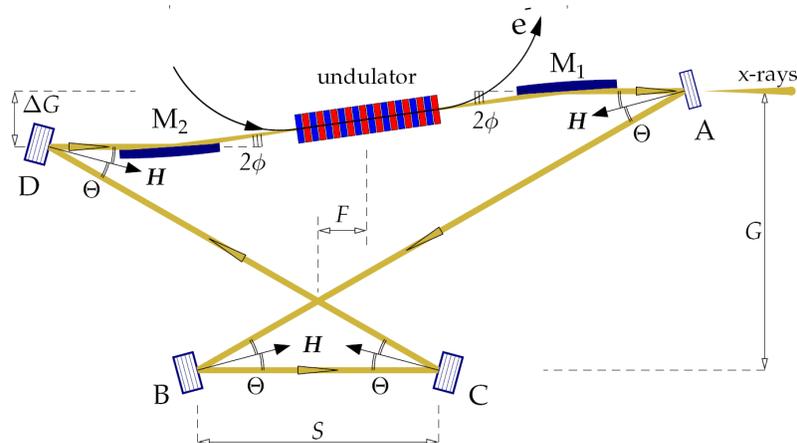


*Figure 9.11  XFELO as a potential candidate for a mode-locked, high-rep-rate source for a hard x-ray frequency comb.*

### 9.5.2 Nuclear States

An alternative is to realize ultra-high-frequency precision from Mössbauer resonance of the low-lying, 7.6 ± 0.5-eV nuclear state in $^{229}$Th, with an estimated natural line width in the range of 0.1 Hz - 10 mHz [49, 50]. This line width is superior to current atomic-clock limits by nearly 4-5 orders of magnitude. The present accuracy in the variation of the fundamental constants are approaching $10^{-15}$ per year utilizing the best atomic clocks, while the $^{229}$Th resonance can deliver a measurement accuracy of about $10^{-20}$ per year. While attempts to perform this nuclear excitation with UV beam from the Advanced Light Source are planned, feeding the resonance by populating the second excited state of 29.19 keV holds much promise. The materials physics and technology problems of realizing this resonance are immense. A worldwide joint effort may be necessary to advance progress.

The technological impact of atomic clocks has been profound, ranging from the successful implementation of global positioning systems and cellular telephones to the synchronization of modern-day electrical power grids. Improved clocks, based on optical frequency standards, are likely to have real-world utility at an even greater level. Furthermore, high-precision clocks have provided a means to probe fundamental issues in physics. For example, atomic clock experiments have provided some of the most stringent tests of General Relativity [51] (see Box 1) and the variability of the fundamental constants [52]. Because of these motivations, there is presently enormous effort towards building next-generation atomic clocks. It appears universally recognized that the most promising route to improved clocks utilizes reference oscillators based on optical transitions. Indeed, several optical atomic clock experiments have already reported better stability than the primary U.S. Cesium standard [52, 53].

Recently, a novel optical frequency standard based on a high-Q transition in the $^{229}$Th nucleus was proposed [55]. This paradigm shift in optical frequency standards is possible because, as indicated by recent data [54], the $^{229}$Th transition has the lowest energy of any known nuclear excitations, making it amenable to study by laser spectroscopy. Furthermore, because nuclear energy levels are relatively insensitive to their environment, the complicated vacuum apparatus of current optical frequency standards can be replaced by a single crystal doped with $^{229}$Th atoms. A thorough analysis of the host crystal environment [55] has shown that clock performance of $\Delta f/f < 10^{-16}$ at 1 s is possible (Fig. 9.12).

In addition to their attractive properties as a frequency standard, nuclear clock systems, due to their large internal interaction energies, open the possibility for even more dramatic improvements in sensitivity to address one of the most interesting questions in fundamental physics: Are the constants of nature actually constant? Recent astrophysical measurements have hinted at possible fundamental constant variation over cosmological time and distance [56]. Moreover, current theories that attempt to unify gravity with the other fundamental forces can lead to spatial and temporal variations in the fundamental constants, e.g., the fine structure constant $\alpha$. These theories can include space-time with extra dimensions of variable geometry, and/or light scalar fields whose variable amplitude couples to ordinary matter. Both effects can change the apparent values of constants. Light scalar fields are potential candidates, dubbed quintessence, to explain the observed dark energy that dominates the universe. Thus, sensitive probes for possible variation of fundamental constants provide an important means to constrain these models, which are extensions to the Standard Model. Finally, as recent

astrophysical measurements have predicted a fractional time variation of the fine-structure constant of $1 \times 10^{-19}$ yr$^{-1}$, the controversy can now be settled with precision laboratory-based measurements at this level. Currently, it appears this level of sensitivity is only reachable with a nuclear clock- based system [55] ($^{229}$Th, $^{235}$U, etc.)

Further, since the performance limit of any clock is set by its transition Q-factor, narrow high-energy nuclear transitions, such as those in $^{235}$U (76 eV) or any of the narrow nuclear transitions that exist above 1 keV, represent the penultimate goal of optical clock work. There are, however, many key challenges to building a high-energy nuclear optical clock, which must be addressed:

-   Mitigation of internal conversion and electron bridge mechanisms

-   Host crystal growth and characterization

-   Better understanding of the shifts and broadenings of a lattice environment (i.e., pushing the science of Mössbauer spectroscopy to the ultra-narrow linewidth regime)



| Nuclide | $^{229}$Th |
|---|---|
| Abundance, (%) | 7340 yrs (100%) |
| Resonance, $E_o$ | 7.6 eV |
| Transition ($I_g$ - $I_e$) | 5/2$^+$ - 3/2$^+$ |
| Multipolarity | M1 |
| $T_{1/2}$ | 26,000 s |
| Bandwidth, $\Gamma$ | 17.5zeV |
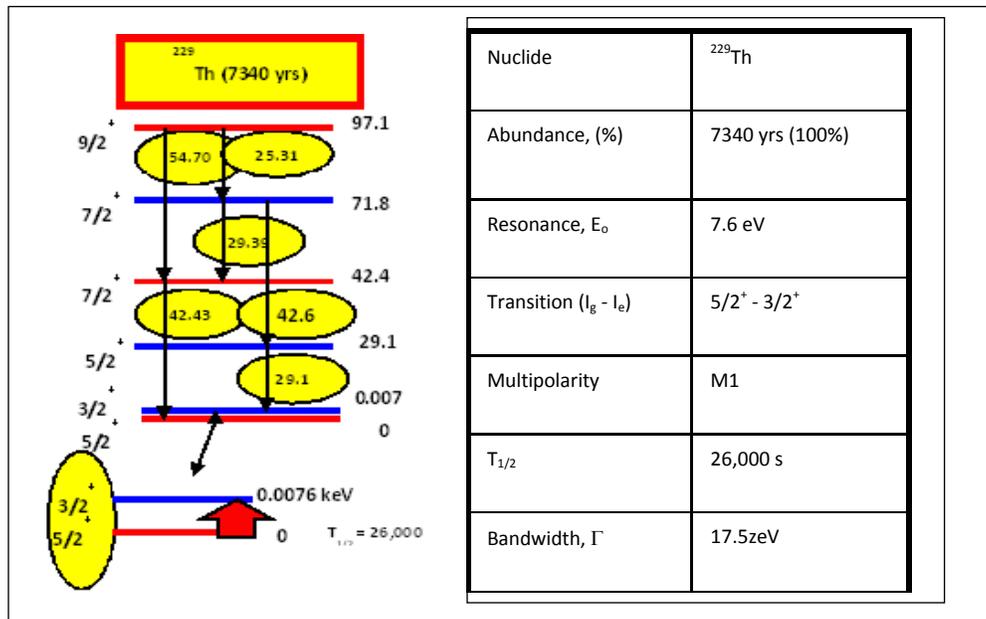
*Figure 9.12  The energy level diagram of $^{229}$Th. The properties of 7.6 eV a resonant state are in the table on the right.*

Work with a thorium-based optical clock, where these challenges are less severe due to the small energy of the nuclear transition, is a necessary first step in these important directions. Other precision measurements that are enabled by high-resolution nuclear spectroscopy are tests of Lorentz invariance via gravitational red-shift measurements, Bose-Fermi symmetry test via violation of super-selection rules, and parity non-conservation test via weak interaction shift of nuclear energy levels.

In summary, this approach, which draws heavily on both atomic, solid-state, and nuclear physics has the possibility for opening a new field of research, solid-state optical nuclear clocks, while simultaneously addressing the need to establish both better physical standards and test the basic laws of physics. It also represents a first step toward ultra-high-resolution Mössbauer spectroscopy that will be enabled by next-generation x-ray sources.

## Way to Test an Einstein Premise Found by 2 Harvard Scientists

Glen A. Rebka Jr.          Prof. Robert V. Pound

By HAROLD M. SCHMECK Jr.

Physicists at Harvard University have found a way of testing conclusively a crucial premise of Einstein's General Theory of Relativity. Heretofore it has always defied measurement, even against the giant yardstick of astronomical space.

In certain gamma rays, which are like high energy X-rays, the physicists have found a tool so sensitive they are sure the prediction can be tested in a single building over a path as short as seventy-five feet.

Such a space is offered by a tower built into the university's red brick Jefferson Physical Laboratory nearly 100 years ago. That was long before gamma rays or relativity had been thought of by the world's scientists.

The authors of the experiment are Dr. Robert V. Pound, a Professor of Physics with a reputation for meticulous research, and Glen A. Rebka Jr., a graduate student working for his doctorate.

They will use gamma rays of very sharply defined wave length to test a basic postulate of Einstein's theory called the principle of equivalence.

The theory holds that there

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# Appendix 1:  Workshop Program

## *Plenary Session, APS Auditorium*
### Oct. 11, 2010, Monday

08:00 – 08:30 **Registration**

08:30 – 08:45 Eric Isaacs, Laboratory Director, Argonne
*Welcome Remarks*

08:45 – 09:00 Gopal Shenoy, Argonne National Laboratory
*Workshop Introduction*

09:00 – 09:30 Sam Bader, Argonne National Laboratory
*Spintronics*

09:30 – 10:00 Todd Hufnagel, Johns Hopkins University
*Evolution of complex microstructures: Opportunities for new experiments with hard x-ray sources*

10:00 – 10:30 **Break**

10:30 – 11:00 Bartosz Grzybowski, Northwestern University
*Chemical Systems: Large and Small*

11:00 – 11:30 Keith Moffat, University of Chicago
*How Do Biomolecules Harness the Energy in a Photon to Generate a Signal?*

11:30 – 12:00 Sidney Nagel, University of Chicago
*Hydrodynamics of Flowing Fluids*

12:00 – 12:30 Ralf Röhlsberger, DESY, Hamburg
*Nonlinear x-ray Physics and Extreme x-ray Metrology*

12:30 – 14:00 **Lunch**

14:00 – 14:30 David E. Moncton, Massachusetts Institute of Technology
*High-Brilliance Compact x-ray Sources: A Small Revolution in x-ray Sources and Applications*

14:30 – 15:00 Harald Reichert, ESRF, Grenoble
*Future of Storage Rings*

15:00 – 15:30 Sol Gruner, Cornell University
*Status of Hard x-ray Energy Recovery Linac (ERL) Light Sources*

15:30 – 16:00 **Break**

16:00 – 16:20 Jerry Hastings, SLAC, Stanford
*Hard x-ray Free Electron Lasers Work: Present Status and Future
Potential*

16:20 – 16:40 Edgar Weckert, DESY, Hamburg
*Status of Hard x-ray FELs*

16:40 – 17:40 *Parallel Sessions / Focus Panels - (Separate Rooms)*

# Focus Panel: Control of Processes in Condensed Systems

**Chairs:**
>**Sam Bader (Argonne National Laboratory)**
>**Paul Evans (University of Wisconsi, Madison**
>**John Freeland (Argonne National Laboratory)**

## Oct. 11, 2010, Monday, Room A1100

17:00 -17:30 **Focus Panel Introductions and Statement of Goals**

## Oct. 12, 2010, Tuesday, Room A1100

### Dynamics and Inhomogeneity in Complex Oxides

08:30 – 09:00 Stephen D. Kevan, University of Oregon
*Nanoscale Intermittency and Emergence in Complex Materials*

09:00 – 09:30 Antonio Bianconi, Department of Physics, Sapienza University of Rome
*Imaging power law distribution of mobile dopant ordering favoring high temperature superconductivity*

09:30 – 10:00 John Freeland, Argonne National Laboratory, Argonne
*Unraveling Phase Transitions in Complex Oxides*

10:00 – 10:30 Paul G. Evans, University of Wisconsin, Madison
*Opportunities in Far-from-Equilibrium Complex Oxide Electronic Materials*

10:30 – 11:00 **Break**

11:00 – 11:30 Joel D. Brock, Cornell University
*Dynamics of Thin-Film Deposition*

11:30 – 12:00 Maya Kiskinova, Sincrotrone Trieste, Trieste
*Challenges for exploring dynamic/transient behaviour of complex nano-objects and new opportunities opened by ultra-bright hard x-rays*

12:00 – 12:30 **Recap, Discussions and Draft Summaries**

12:30 – 14:00 **Lunch**

### Controlling Magnetism with Light

14:00 – 14:30 Gerardo Bertero, Western Digital Corporation
*Extending Magnetic Recording Areal Densities into the Tb/square-inch range*

14:30 – 15:00 Michel van Veenendaal, Northern Illinois University, De Kalb, IL and ANL
*Time-Dependent x-ray spectroscopy as a Probe of Ultrafast Dynamics in Transition-Metal Photo-excited Complexess*

15:00 – 15:30 A. V. Kimel, Radboud University Nijmegen, Nijmegen, The Netherlands
*Magnetism on a time-scale of exchange interaction*

15:30 – 16:00 **Break**

16:00 – 16:30 **Recap, Discussions and Draft Summaries**

## Coherent Probes for Dynamics

16:30 – 17:00 Bruce D. Patterson, SwissFEL Project, Paul Scherrer Institut
*Time-Resolved Stimulated x-ray Raman Scattering*

17:00 – 17:30 Ivan A. Vartanyants, Deutsches Electronen-Synchrotro Hamburg
*Theory of cross-correlation analysis in disordered systems*

17:30 – 18:00 **Recap, Discussions and Draft Summaries, Writing Assignments**


## Oct. 13, 2010, Wednesday, Room A1100

## Nanomagnetism

08:30 – 09:00 Susan Coppersmith, University of Wisconsin, Madison
*The frontier of spin coherence in silicon nanostructures*

09:00 – 09:30 Byoung-Chu Choi, University of Victoria, Canada
*Vortex Dynamics in Multilayered Nanopillar Element − Spin-Transfer Torque Magnetic Random Access Memory (STT-MRAM)*

09:30 – 10:00 Oleg Shpyrko, University of California at San Diego
*Probing complex magnetic domains via coherent x-ray diffractive imaging*

10:00 – 10:30 **Break**

10:30 – 12:00 **Focus Panel: Summary Presentation Preparation**

## Oct. 13, 2010, Wednesday, Plenary Session, 401 Auditorium

13:30 – 15:15 **Summary Presentations from Focus Panels** (15 minutes each)

15:15 – 15:30 **Workshop Summary**

15:30 **Adjourn**

# Focus Panel: Controlling the Dynamics of Materials Processing

**Chairs:**

      **Todd Hufnagel (John Hopkins University)**
      **Alan Godman (Ames Laboratory and Iowa State University) and**
      **Jonathan Almer (Argonne National Laboratory)**

## Oct. 11, 2010, Monday Room E1100/E1200

17:00 -17:30 **Focus Panel Introductions and Statement of Goals**

## Oct. 12, 2010, Tuesday Room E1100/E1200

### Evolution of Complexity in Materials

08:30 – 09:00 Ben Larson, Oak Ridge National Laboratory
*Probing Complexity in Nonequilibrium Materials Processing*

09:00 – 09:30 Alan I. Goldman, Ames Laboratory and Iowa Sate University
*Using Electrostatic Levitation and High-energy x-ray Diffraction to Probe the Nature of Deeply Supercooled Liquids*

09:30 – 10:00 Gabrielle Long, Argonne National Laboratory
*Metallic or semiconducting liquid silicon under swift heavy ion (SHI) irradiation*

10:00 – 10:30 **Recap, Discussions and Draft Summaries**

10:30 – 11:00 **Break**

### Disordered and Reactive Dynamics

11:00 – 11:30 Subramanian Sankaranarayanan, Center for Nanoscale Materials, ANL
*Atomic Scale Electric Field Control of the Structure and Morphology of a Growing Ultra-Thin Oxide Film*

11:30 – 12:00 Paul H. Fuoss, Argonne National Laboratory
*Nonlinear Dynamics and the Reactive Synthesis of InN*

12:00 – 12:30 Christian Gutt, DESY, Hamburg
*Detecting and quantifying local symmetries in disordered materials via speckle fluctuations*

12:30 – 14:00 **Lunch**

14:00 – 14:30 Jonathan Almer, Argonne National Laboratory
*Opportunities for studies of complex materials using high-energy x-rays*

14:30 – 15:00 **Recap, Discussions and Draft Summaries**

### Informatics and Simulation

15:00 – 15:30 Krishna Rajan, Iowa State University, Ames
*Informatics for Discovering the "Inorganic Gene" in Complex Inorganic Solids*

15:30 – 16:00 **Break**

16:00 – 16:30 Danny Perez, Los Alamos National Laboratory
*Bridging the timescale gap between simulations and experiments using Accelerated Molecular Dynamics*

16:30 – 17:00 Daniel Hooks, Los Alamos National Laboratory
*Material state and damage evolution in dynamic loading*

17:00 – 17:30 **Recap, Discussions and Draft Summaries, Writing Assignments**

## Oct. 13, 2010, Tuesday Room E1100/E1200

08:30 – 10:00 **Focus Panels: Summary Preparation and Editing Assignments**

10:00 – 10:30 **Break**

10:30 – 12:00 **Focus Panels: Summary Presentation Preparation**

12:00 – 13:30 **Lunch**

## Oct. 13, 2010, Wednesday, Plenary Session, 401 Auditorium

13:30 – 15:15 **Summary Presentations from Focus Panels** (15 minutes each)

15:15 – 15:30 **Workshop Summary**

15:30 **Adjourn**

# Focus Panel: Nonlinear Chemical Reactions

**Chairs:**
> **Lin Chen (Argonne/Northwestern University)**
> **Simone Techert (Max Planck Institute, Goettingen)**
> **David Tiede (Argonne National Laboratory)**

## Oct. 11, 2010, Monday, Room B3100

17:00 -17:30 **Focus Panel Introductions and Statement of Goals**

## Oct. 12, 2010, Tuesday, Room B3100

### Complexity of Energy Conversion Dynamics

08:30 – 09:00 Lin X. Chen, Argonne Nat'l Laboratory and Northwestern University
*Electronic Coherence in Solar Energy Conversion Processes in Transition Metal Complexes: Visualization and Control*

09:00 – 09:30 Daniel Friebel, SLAC, Stanford
*Spectroscopy on catalyst surfaces in high pressure gas or liquid environment*

09:30 – 10:00 David M. Tiede, Argonne National Laboratory
*Structural Dynamics Challenges in Photosynthesis and Molecular Solar Fuels Catalysis*

10:00 – 10:30 Break

10:30 – 11:00 Christian Bressler, European XFEL GmbH, Hamburg
*Femtosecond Spin State Changes – Implications for Photocatalysis*

11:00 – 11:30 Larry A. Curtiss, Argonne National Laboratory
*First principles studies of nanoscale effects on catalytic activity and selectivity*

11:30 – 12:00 **Recap, Discussions and Draft Summaries**

### Coherent Control and Reacting Systems

12:00 – 12:30 Linda Young, Argonne National Laboratory
*Extending coherent control to complex systems*

12:30 – 14:00 **Lunch**
14:00 – 14:30 Tamar Seideman, Northwerstern University
*Laser Elighnment in Complex Media*

14:30 – 15:00 Stephen T. Pratt, Argonne National Laboratory
*x-ray Probes of Electronic Structure in Reacting Systems*

15:00 – 15:30 Marcos Dantus, Michigan State University
*Using computer controlled ultrafast laser pulses to control matter*

15:30 – 16:00 **Break**

16:00 – 16:30 Steven J. Sibener, The University of Chicago
*Chemical Imaging and Dynamical Studies of Complex Interfacial Systems*

16:30 – 17:00 **Recap, Discussions and Draft Summaries**

## Evolution of Environmental Systems

17:00 – 17:30 Young-Shin Jun, Washington University in St. Louis
*Observations of Chemical Evolution in Environmental Systems*

17:00 – 17:30 Richard A Rosenberg, Argonne National Laboratory
*Probing electron-induced chemistry with x-rays* (Bio, Abstract, Ta**lk)**

17:30 – 18:00 **Recap, Discussions and Draft Summaries, Writing Assignment**

## Oct. 13, 2010, Wednesday, Room B3100

## Chemical Dynamics and Phase Transitions

08:30 – 09:00 Simone Techert, Max Planck Institute for Biophysical Chemistry, Goettingen
*Chemical Reactions Studied with Ultrafast x-ray Pulses: From Orbital Movements to Molecular Machines*

09:00 – 09:30 H. Cailleau, Université de Rennes 1, Rennes Cedex
**Evolution and Control of Photoinduced Transformations In Molecular Materials : Experiments for Tracking and Understanding their Non-Equilibrium Cooperative and Coherent Dynamics**

09:30 – 10:00 C. Rose-Petruck, Brown University, Providence
*Ultrafast structural dynamics of solvated organometallic complexes and prospects for studying coherent bi-molecular reactions*

10:00 – 10:30 **Break**

10:30 – 12:00 **Recap and Focus Panels: Summary Preparation and Editing Assignments**

12:00 – 13:30 **Lunch**

## Oct. 13, 2010, Wednesday, Plenary Session, 401 Auditorium

13:30 – 15:15 **Summary Presentations from Focus Panels** (15 minutes each)

15:15 – 15:30 **Workshop Summary**

15:30 **Adjourn**

# Focus Panel: Controlling Biological Functions

**Chairs:**
> **Sol Gruner (Cornell)**
> **Ian McNulty (Argonne National Laboratory)**

## Oct. 11, 2010, Monday Room B2100

16:40 -17:10 **Focus Panel Introductions and Statement of Goals**

17:10 – 17:40 Chris Jacobsen, Argonne Nat'l Lab and Northwestern University
*x-ray microscopy: freezing complex biological processes*

## Oct. 12, 2010, Tuesday Room B2100

### Future Vision for Biology

08:30 – 09:00 Sol M. Gruner, Cornell University
*Some Grand Challenges in Synthetic Biology*

09:00 – 09:30 Ilme Schlichting, Max Planck Institute for Medical Research, Heidelberg
*FELs - emerging opportunities in structural biology*

09:30 – 10:00 John C.H. Spence, Arizona State University
*Femtosecond nanodiffraction using a hard x-ray laser*

10:00 – 10:30 **Recap, Discussions and Draft Summaries**

10:30 – 11:00 **Break**

11:00 – 11:30 Marius Schmidt, University of Wisconsin, Milwaukee
*Energetics of Biological Macromolecules from Five-Dimensional Crystallographic Data*

11:30 – 12:00 Peter Schwander , University of Wisconsin-Milwaukee
*Structure and its Variations from Random Low-Signal Snapshots*

12:00 – 12:30 **Recap, Discussions and Draft Summaries**

12:30 – 14:00 **Lunch**

### Protein Dynamics and Folding

14:00 – 14:30 Soichi Wakatsuki , Photon Factory, Structural Biology Research Center
*Biological nanomachines and their control*

14:30 – 15:00 A.C. McIntosh, ERRI, SPEME, University of Leeds
*Suggestions for experimental work concerning the protein folding*

15:00 – 15:30 Karl F. Freed, University of Chicago

*Protein Folding: Predicting Structure from Sequence*

15:30 – 16:00 **Break**

16:30 – 17:00 Sebastian Doniach, Stanford University
*Use of correlated xray scattering (CXS) to track protein motions during enzyme catalysis by means of an xray freeelectron laser*

17:00 – 17:30 Andrew H. Marcus, University of Oregon, Eugene
*Controlling Structure and Energy Transfer in Liposome Ordered Porphyrin Aggregates by Fluorescence-Detected 2D Electronic Spectroscopy*

17:30 – 18:00 **Recap, Discussions and Draft Summaries, Writing Assignments**

## Oct. 13, 2010, Tuesday Room B2100

## Towards Organismal Biology

08:30 – 09:00 Lee Makowski, Northeastern University, Boston
*Probing Protein Ensembles and Functional Intermediates with x-ray Solution Scattering*

09:00 – 09:30 Keith C. Cheng, Penn State Hershey College of Medicine, Hershey
*Defining the Phenomic Landscape for Genes, Chemicals, and Diseases*

09:30 – 10:00 **Focus Panels: Summary Preparation and Editing Assignments**

10:00 – 10:30 **Break**

10:30 – 12:00 **Focus Panels: Summary Presentation Preparation**

12:00 – 13:30 **Lunch**

## Oct. 13, 2010, Wednesday, Plenary Session, 401 Auditorium

13:30 – 15:15 **Summary Presentations from Focus Panels** (15 minutes each)

15:15 – 15:30 **Workshop Summary**

15:30 **Adjourn**

# Focus Panel: Dynamics in Softmatter and Fluidics

**Chairs:**
>    **Jin Wang (Argonne National Laboratory)**
>    **Wah Keat Lee (Argonne National Laboratory)**


## Oct. 11, 2010, Monday Room B2100

17:00 -17:30 **Focus Panel Introductions and Statement of Goals**


## Oct. 12, 2010, Tuesday Room B2100


### Micro- and Nanofluidics

08:30 – 09:00 Sarah Köster, Max Planck Institute for Dynamics and Self-Organization,
Göttingen
*x-ray Studies of Bio-Matter in Microfluidic Sample Environments*

09:00 – 09:30 Hsueh-Chia Chang, University of Notre Dame
*A New Nucleic Acid Detection Platform based on Nanofluidics : Exploiting Non-Equilibrium Ion Distribution and DNA ConformationDynamics*

09:30 – 10:00 Kamel Fezzaa, Argonne National Laboratory, Argonne
**Fluid dynamics: High-speed x-ray full-field imaging**

10:00 – 10:30 Aaron Streets, Stanford University
*Microfluidic Large-Scale Integration*

10:30 – 11:00 **Break**

11:00 – 11:30 Randall E. Winans, Argonne National Laboratory
*Small Angle x-ray Studies of Particle in Flames*
11:30 – 12:00 **Recap, Discussions and Draft Summaries**


### Soft Matter Dynamics
12:00 – 12:30 Ka Yee C. Lee, The University of Chicago
*Beyond Wrinkling: Stress Relaxation in Lung Surfactant Monolayers and Other Elastic Thin Films*

12:30 – 14:00 **Lunch**

14:00 – 14:30 Millicent (Millie) A. Firestone, Argonne National Laboratory
*Soft Nanostructured Materials*

14:30 – 15:00 Binhua Lin, The University of Chicago
*Soft Nanostructured Materials*

15:00 – 15:30 **Recap, Discussions and Draft Summaries**

15:30 – 16:00 **Break**

## Dynamics of Disordered Materials

16:00 – 16:30 Mark Sutton, McGill University
*Use of heterodyne and homodyne x-ray photon correlation spectroscopy to measure velocity distributions*

16:30 – 17:00 C. Gutt, DESY, Hamburg
*Detecting and quantifying local symmetries in disordered materials via speckle fluctuations*
17:00 – 17:30 Laurence Lurio, Northern Illinois University
*Alpha Crystallin Diffusion in Concentrated Suspensions*

17:30 – 18:00 **Recap, Discussions and Draft Summaries, Writing Assignments**

## Oct. 13, 2010, Tuesday Room B2100

## Complexity of Functions in Large Systems

08:30 – 09:00 Konstantin G. Kornev, Clemson University
*Evolution and control of complexity: from butterfly proboscis to artificial probes for single cell analyses*

09:00 – 09:30 Andy C. McIntosh, ERRI, SPEME, University of Leeds
*Suggestions for experimental work concerning the bombardier beetle*

09:30 – 10:00 **Recap, Discussions and Draft Summaries**

10:00 – 10:30 **Break**

10:30 – 12:00 **Focus Panel: Summary Presentation Preparation**

12:00 – 13:30 **Lunch**

## Oct. 13, 2010, Wednesday, Plenary Session, 401 Auditorium

13:30 – 15:15 **Summary Presentations from Focus Panels** (15 minutes each)

15:15 – 15:30 **Workshop Summary**

15:30 **Adjourn**

# Focus Panel: Nonlinear X-ray Science and Extreme X-ray Metrology

**Chairs:**
> **Ralf Roelsberger (DESY)**
> **Joerg Evers (MPI - Kernphysik, Heidelberg)**
> **Bernhard Adams (Argonne National Laboratory)**

## Oct. 11, 2010, Monday Room A5000

16:40 –17:10 *Focus Panel Introductions and Statement of Goals*

17:10 – 17:40 Eric R. Hudson, UCLA
*Frequency reference based on the 229-Th nucleus*

## Oct. 12, 2010, Tuesday Room A5000

### Non-linear Science

08:30 – 09:00 Bernhard Adams, Argonne National Laboratory
*Nonlinear Optics and Quantum Optics with x-rays*

09:00 – 09:30 Kenij Tamasaku, RIKEN SPring-8 Center, Hyogo, Japan
*Recent progress in x-ray nonlinear optics and future perspectivesStimulated Inelastic x-ray Scattering*

09:30 – 10:00 Bruce D. Patterson, SwissFEL Project, Paul Scherrer Institut, Villigen
*Time-Resolved Stimulated x-ray Raman Scattering*

10:00 – 10:30 **Recap, Discussions and Draft Summaries**

10:30 – 11:00 **Break**

### Controlling Longitudinal Coherence

11:00 – 11:30 Kwang-Je Kim, Argonne National Laboratory, Argonne

*x-ray FEL oscillator: Performance and feasibility*

11:30 – 12:00 G. Geloni, European XFEL GmbH, Hamburg
*Self-seeding techniques for hard x-ray FELs*

12:00 – 12:30 **Recap, Discussions and Draft Summaries**

12:30 – 14:00 **Lunch**

### Entanglement and Cooperative Emission

14:00 – 15:00 Joerg Evers, Max-Planck-Institut fur Kernphysik, Heidelberg
*Generation and detection of x-ray entanglement*

14:30 – 15:00 Marlan Scully, Texas A&M and Princeton University
*Collective Lamb shift in single-photon superradiance*

15:00 – 15:30 **Recap, Discussions and Draft Summaries**

15:30 – 16:00 **Break**

## Extreme Metrology

16:00 – 17:00 Tom K. Allison, JILA, NIST, University of Colorado, Boulder
*The EUV frequency comb and prospects for x-ray combs* (Bio, Abstract, Talk)

17:00 – 17:30 **Recap, Discussions and Draft Summaries, Writing Assignments**

## Oct. 13, 2010, Tuesday Room A5000

## Quantum Control and Metrology

08:30 – 09:00 Adriana Palffy, Max Planck Institute for Nuclear Physics, Heidelberg
*Quantum control of nuclei with coherent x-ray light* (Bio, Abstract, Talk)

09:00 – 09:30 Daniel López, Center for Nanoscale Materials, Argonne Nat'l Laboratory
*Near field interactions in nanoscale science* (Bio, Abstract, Talk)

09:30 – 10:00 **Focus Panels: Summary Preparation and Editing Assignments**

10:00 – 10:30 **Break**

10:30 – 12:00 **Focus Panels: Summary Presentation Preparation**

12:00 – 13:30 **Lunch**

## Oct. 13, 2010, Wednesday, Plenary Session, 401 Auditorium

13:30 – 15:15 **Summary Presentations from Focus Panels** (15 minutes each)

15:15 – 15:30 **Workshop Summary**

15:30 **Adjourn**

# Appendix 2: Workshop Participants

| Name | Institution |
|---|---|
| **Name** | **Institution** |
| Adams, Bernhard W. | Argonne National Laboratory |
| Allison, Thomas K. | JILA |
| Almer, Jonathan D. | Argonne National Laboratory |
| Alp, Esen Ercan | Argonne National Laboratory |
| Assoufid, Lahsen | Argonne National Laboratory |
| Bader, Samuel D. | Argonne National Laboratory |
| Banerjee, Arnab | The University of Chicago |
| Beno, Mark A. | Argonne National Laboratory |
| Bergmann, Uwe | SLAC National Accelerator Laboratory |
| Bertero, Gerardo A. | Western Digital Corporation |
| Bianconi, Antonio | Sapienza Università di Roma |
| Borland, Michael D. | Argonne National Laboratory |
| Boutet, Sebastien F. | SLAC National Accelerator Laboratory |
| Bressler, Christian G. | European XFEL GmbH |
| Brinkmann, Reinhard | Deutsches Elektronen Synchrotron |
| Brock, Joel D. | Cornell University |
| Brown, Eric Nathaniel | Los Alamos National Laboratory |
| Cailleau, Herve | University Rennes 1 |
| Chang, Hsueh-Chia | University of Notre Dame |
| Chen, Lin X. | Argonne National Laboratory and Northwestern University |
| Chen, Yu-Sheng | The University of Chicago |
| Choi, Byoung-Chul | University of Victoria |
| Coppersmith, Susan N. | University of Wisconsin-Madison |
| Crabtree, George W. | Argonne National Laboratory |
| Croft, Mark C. | Rutgers University |
| Cross, Julie O. | Argonne National Laboratory |
| Curtiss, Larry A. | Argonne National Laboratory |
| D'Amico, Kevin L. | Washington State Universiry |
| Dagotto, Elbio R. | University of Tennessee |
| Dantus, Marcos | Michigan State University |
| Davey, Steve | Argonne National Laboratory |
| Doniach, Sebastian | Stanford University |
| Dosch, Helmut | Deutsches Elektronen Synchrotron |
| Dufresne, Eric M. | Argonne National Laboratory |
| Dunham, Bruce M. | Cornell University |
| Durr, Hermann A. | SLAC National Accelerator Laboratory |
| Evans, Paul G. | University of Wisconsin-Madison |
| Evers, Jörg | Max-Planck-Institut für Kernphysik |
| Fezzaa, Kamel | Argonne National Laboratory |

| Name | Institution |
|---|---|
| Freed, Karl F. | The University of Chicago |
| Freeland, John W. | Argonne National Laboratory |
| Freelon, Byron K. | Lawrence Berkeley National Laboratory |
| Friebel, Daniel | SLAC National Accelerator Laboratory |
| Fuoss, Paul H. | Argonne National Laboratory |
| Gagyi Palffy, Adriana  Claudia | Max Planck Institute Heideberg |
| Geloni, Gianluca | European XFEL GmbH |
| Goldman, Alan Ira | Iowa State University and Ames Laboratory |
| Graber, TImothy J. | The University of Chicago |
| Gruner, Sol M. | Cornell University |
| Grzybowski, Bartosz Andrzej | Northwestern University |
| Gutt, Christian | Deutsches Elektronen Synchrotron |
| Haeffner, Dean | Argonne National Laboratory |
| Hajdu, Janos | Uppsala University |
| Hastings, Jerome | SLAC National Acclerator Laboratory |
| Hettel, Robert O. | SLAC National Accelerator Laboratory |
| Hooks, Daniel E. | Los Alamos National Laboratory |
| Hudson, Eric R. | University of California, Los Angeles |
| Hufnagel, Todd C. | Johns Hopkins University |
| Ilavsky, Jan | Argonne National Laboratory |
| Isaacs, Eric D. | Argonne National Laboratory |
| Jacobsen, Chris J. | Argonne National Laboratory |
| Jun, Young-Shin | The Washington University |
| Kevan, Stephen D. | University of Oregon |
| Khounsary, Ali | Argonne National Laboratory |
| Kim, Kwang-Je | Argonne National Laboratory |
| Kimel, Alexey V. | Radboud University Nijmegen |
| Kiskinova, Maya Petrova | Sincrotrone Trieste |
| Koester, Sarah F. | Georg-August-University Goettingen |
| Kornev, Konstantin G. | Clemson University |
| Lai, Ming-Chia Daniel | Wayne State University |
| Lal, Jyotsana | Argonne National Laboratory |
| Lang, Jonathan C. | Argonne National Laboratory |
| Larson, Bennett C. | Oak Ridge National Laboratory |
| Lee, Ka Yee C. | The University of Chicago |
| Lee, Wah-Keat | Argonne National Laboratory |
| Lin, Binhua | The University of Chicago |
| Lindau, Ingolf Evert | SLAC National Accelerator Laboratory |
| Lindenberg, Aaron M. | Stanford University |
| Long, Gabrielle G. | Argonne National Laboratory |
| Lopez, Daniel O. | Argonne National Laboratory |
| Lu, Zheng-Tian | Argonne National Laboratory |

| Name | Institution |
|---|---|
| Makowski, Lee | Argonne National Laboratory |
| Mancini, Derrick C. | Argonne National Laboratory |
| Marcus, Andrew H. | University of Oregon |
| Marshall, Matthew Joseph | Pacific Northwest National Laboratory |
| McIntosh, Andy C. | University of Leeds |
| McNulty, Ian Laurence | Argonne National Laboratory |
| Mills, Dennis M. | Argonne National Laboratory |
| Mitchell, John F. | Argonne National Laboratory |
| Moffat, Keith | The University of Chicago |
| Moncton, David E. | Massachusetts Institute of Technology |
| Narayanan, Theyencheri | European Synchrotron Radiation Facility |
| Nielsen, Martin Meedom | Technical University of Denmark |
| Noonan, John | Argonne National Laboratory |
| Norman, Michael R. | Argonne National Laboratory |
| Ourmazd, Abbas | University of Wisconsin, Milwaukee |
| Patterson, Bruce D. | Paul Scherrer Institute |
| Pellegrini, Claudio | University of California, Los Angeles |
| Perez, Danny | Los Alamos National Laboratory |
| Pratt, Stephen T. | Argonne National Laboratory |
| Rajan, Krishna | Iowa State University |
| Reichert, Harald M. | European Synchrotron Radiation Facility |
| Röhlsberger, Ralf | Deutsches Elektronen Synchrotron |
| Rose-Petruck, Christoph G. | Brown University |
| Rosenbaum, Gerold A. | University of Georgia and Argonne National Laboratory |
| Rosenberg, Richard A. | Argonne National Laboratory |
| Ryan, Philip J. | Argonne National Laboratory |
| Sandy, Alec | Argonne National Laboratory |
| Sankaranarayanan, Subbu | Argonne National Laboratory |
| Sarrao, John L. | Los Alamos National Laboratory |
| Schlichting, Ilme Elisabeth | Max Planck Institute for medical Research |
| Schmidt, Marius | University of Wisconsin, Milwaukee |
| Schneider, Jochen R. | Deutsches Elektronen Synchrotron |
| Schwander, Peter | University of Wisconsin, Milwaukee |
| Scully, Marlan O. | Texas A&M University and Princeton University |
| Seideman, Tamar | Northwestern University |
| Shastri, Sarvjit D. | Argonne National Laboratory |
| Shen, Guoyin | Carnegie Institution of Washington |
| Shen, Zhixun | Stanford University |
| Shenoy, Gopal | Argonne National Laboratory |
| Shpyrko, Oleg G. | University of California, San Diego |
| Shvyd'ko, Yuri | Argonne National Laboratory |

| Name | Institution |
|---|---|
| Sibener, Steven J. | The University of Chicago |
| Spence, John Charles | Arizona State University |
| Srajer, George | Argonne National Laboratory |
| Stephenson, Brian | Argonne National Laboratory |
| Stohr, Joachim | SLAC National Accelerator Laboratory |
| Streets, Aaron M. | Stanford University |
| Sturhahn, Wolfgang | Jet Propulsion Laboratory |
| Sutton, Mark | McGill University |
| Tamasaku, Kenji | RIKEN |
| Techert, Simone Agnes | Max Planck Institute Goettingen |
| Terminello, Louis J. | Pacific Northwest National Laboratory |
| Tessema, Guebre Xabiher | National Science Foundation |
| Tiede, David M. | Argonne National Laboratory |
| Tschentscher, Thomas C. | European XFEL GmbH |
| van Veenendaal, Michel A. | Argonne National Laboratory and Northern Illinois University |
| Vartaniants, Ivan A. | Deutsches Elektronen Synchrotron |
| Viccaro, P. James | The University of Chicago |
| Wakatsuki, Soichi | High Energy Accelerator Research Organization, KEK |
| Walker, Richard P. | Diamond Light Source Ltd. |
| Wang, Jin | Argonne National Laboratory |
| Wang, Luhong | Argonne National Laboratory |
| Weckert, Edgar Franz | Deutsches Elektronen Synchrotron |
| Wen, Haidan | Argonne National Laboratory |
| Winans, Randall E. | Argonne National Laboratory |
| Xiao, Yuming | Carnegie Institution of Washington |
| Yarin, Alexander | University of Illinois at Chicago |
| You, Hoydoo | Argonne National Laboratory |
| Young, Linda | Argonne National Laboratory |
| Zholents, Alexander A. | Argonne National Laboratory |
| Zschack, Paul | Argonne National Laboratory |

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