ULTRAFAST SCIENCE OPPORTUNITIES WITH ELECTRON MICROSCOPY

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Ultrafast Science Opportunities with Electron Microscopy

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X-rays and electrons are two of the most fundamental probes of matter. When the Linac Coherent Light Source (LCLS), the world's first x-ray free electron laser, began operation in 2009, it transformed ultrafast science with the ability to generate laser-like x-ray pulses from the manipulation of relativistic electron beams. This document describes a similar future transformation. In Transmission Electron Microscopy, ultrafast relativistic (MeV energy) electron pulses can achieve unsurpassed spatial and temporal resolution. Ultrafast temporal resolution will be the next frontier in electron microscopy and can ideally complement ultrafast x-ray science done with free electron lasers. This document describes the Grand Challenge science opportunities in chemistry, material science, physics and biology that arise from an MeV ultrafast electron diffraction & microscopy facility, especially when coupled with linac-based intense THz and X-ray pump capabilities.

Complementarity of x-rays and electrons: Electrons have a larger scattering cross-section compared to x-rays but a smaller sample damage (inelastic scattering) cross section (Fig. 1). They are particularly well suited for studying dilute samples and allow for real space imaging. While the small de Broglie wavelength of electrons allow them to cover a large q-space, x-rays offer generally higher q-space resolution. The challenge for improving the temporal resolution of ultrashort electron pulses is to overcome the repulsive Coulomb interaction, i.e. the space-charge effects. This is where accelerator technology developed for XFELs can play a decisive role. An ultrafast electron diffraction & microscopy facility at SLAC can take advantage of the recent developments in high-brightness ultrafast (MeV) electron sources, in high-field magnets and in electron detection, thus, minimizing space-charge effects [Wang 1996]. This allows more electrons to be packed into each bunch, offering single-shot capabilities similar to those of x-rays from LCLS. A further important advantage of relativistic beams is that they eliminate the velocity mismatch between the electro-magnetic pump pulses and the probe electron beam. This mismatch limits the time resolution of ultrafast dynamics for dilute samples, such as gas and liquid samples [Hensley 2013]. In addition to the higher temporal resolution, MeV electrons can penetrate thicker samples. Finally, the higher electron beam energy leads to a larger elastic scattering cross section and a decrease in the inelastic scattering cross sections [Bhattacharya (1980)], increasing the diffraction signal and reducing inelastic scattering.

Fig.1: Comparison of x-ray and electron scattering cross section (from Quarterly Review of Biophysics **28**, 171-193(1995)).

Figure 2 visualizes the complementarity of (soft) x-rays from LCLS and a MeV electron diffraction & microscopy facility based on the principles outlined above. X-ray holography and phase retrieval using coherent x-ray scattering allows ~ 10 nm spatial resolution in imaging spin [Wang 2013] and in the future, will probe electronic ordering phenomena. Ultrafast electron pulses will revolutionize time resolved imaging of lattice structures on the nm length scale by either using a scanning (see Fig. 2 right) or full-field approach.

Fig.2: Illustration of the complementarity of soft x-rays to image the spin [Wang 2013] and electronic structure (left) and electrons to image the lattice structure (right). Similar cross sections for both probes will enable measurements on the same samples.

We envision a MeV UED&UEM facility to possess the following capabilities:

- **Ultrafast electron diffraction (UED)** will be capable of kHz operation with sub-100 fs temporal resolution. The MeV electron source developed for this application will have both transverse and longitudinal coherent lengths larger than 10 nm. The relativistic electron beam will eliminate the time resolution limit due to the velocity mismatch between the pump laser and the electron probe. Further development could push the temporal resolution down to the order of 10 fs.
- **Nano-UED** with a strong condenser lens and electron beam emittance below nm-rad will enable an electron beam focus on the sample down to 10-nm spot size with 100-fs time resolution. The SLAC nano-UED will represent a paradigm shift as it opens up complementary measurements on the same samples of nanoscale lattice dynamics with nano-UED and of charge/spin dynamics at LCLS using soft x-ray holography. It can provide deep insights into the mechanisms of the lattice response for a wide range of quantum materials and nanostructures. It will be the stepping stone for the development of full-field microscopy (UEM).
- **Ultrafast full-field Electron Microscopy (UEM)** will be capable of single-shot real space imaging with spatial-temporal resolution of 10 nm-10 ps [Xiang_2014]. There is strong scientific interest to further improve the UEM spatial resolution down to 1 nanometer and possibly below. The UEM instrument will provide the R&D platform for achieving even higher spatial resolution by exploring the following two possibilities: improving the spatial resolution down to 1 nm without sacrificing the temporal resolution; or improving the spatial resolution further to ~ 0.3 nm with time resolution ~ 100 ps for biological process imaging.

The combination of LCLS and UED/UEM will provide a broad scientific community with the unique ability to image both structure and function. It will open new frontiers to address the Grand Challenges for Science and the Imagination [BES 2007]:

- I. How do remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and how can we control these properties?*
- II. How do we control material processes at the level of electrons?*
- III. How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?*
- IV. How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things?*
- V. How do we characterize and control matter away— especially very far away —from equilibrium?*

The science enabled by MeV UED/UEM is broad, transformative and crossing a range of fields. They include driving condensed matter systems and warm dense matter far from equilibrium, and probing dynamical effects in gas phase reactions to better understand the molecular energy conversion process. The direct imaging of phonon transport at the nanoscale and single-shot nanoscale nucleation events associated with phase transitions will enable us to master energy and information at the nanoscale. The transformative knowledge gained will enable a more efficient, top-down design and synthesis of revolutionary new forms of matter with tailored properties, with the ultimate goal to create new technologies with capabilities rivaling those of living things. A revolutionary ultrafast electron imaging instrument would allow, for the first time, direct imaging of biologically important conformational transitions of macromolecules and their assemblies in real time. At present, these can only be inferred from indirect spectroscopic or scattering methods. In the following we present the scientific thrusts that map loosely onto the Grand Scientific Challenges listed above:

- 1. THz control of emergence in quantum materials**
- 2. Understanding Non-Born-Oppenheimer dynamics in molecules**
- 3. Matter far from equilibrium: Warm dense matter**
- 4. Nanoscale materials science**
- 5. Towards sub-nanometer imaging of biological processes**
- 6. Understanding nanoscale spatio-temporal correlations of glasses**

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1. THz control of emergence in quantum materials

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Summary: One of the grand challenges in modern condensed matter physics research is to understand and ultimately control the emergence of novel quantum states. We propose to use ultrafast electron diffraction and microscopy to probe the lattice response as strongly correlated electron materials are driven into novel transient states by tailored THz excitation. In combination with complementary probes of the electronic system using XFEL radiation on the same samples, this could lead to a recipe of how to control complex materials' properties in the time domain.

Scientific background: Strongly correlated electron systems are characterized by the competition between various degrees of freedom such as spin, orbital, charge and lattice. This makes these systems very sensitive to external perturbations which has long been thought of as a pathway to control the spectacular materials properties such as high temperature superconductivity, colossal magnetoresistance, insulator-metal transitions and ferroelectrics, i.e. the coupling between magnetic and electric polarization. Experiments so far have mainly explored the use of optical excitation and using LCLS as a probe has been transformative [Lee 2012, de Jong 2013]. However, the relevant energy scale for controlling emergence is far below optical excitations in the THz frequency range. This raises the interesting prospect of controlling materials' properties via THz excitation. Groundbreaking experiments reported the emergence of superconducting [Fausti 2011] and metallic [Rini 2007] behavior out of the insulating materials' phases by resonant excitation of THz lattice vibrations. Understanding and ultimately controlling the microscopic pathways that lead to such exotic behavior will be one of the grand challenges of materials physics in the coming decades. The timely combination of ultrafast electron diffraction and accelerator based THz sources can lead the way as outlined below.

Fig. 3: Schematic illustration of how the electric field control of materials' electrical conductivity could shape future oxide electronics applications (left) and facilitate information storage in ferroelectric heterostructures (right).

Insulator-metal transitions: Motivated by the prospect of novel oxide electronics devices (see Fig. 1) the use of intense half cycle THz pulses has recently been shown to facilitate the transition from insulating to metallic electrical transport in VO₂, one of the prototypical correlated oxide materials displaying insulator-metal transitions in thermal equilibrium [Liu 2012]. One of the central open questions relates to the mechanism underlying field-driven insulator-metal transitions. If novel quantum tunneling [Schiffrin, 2013] is the driving force it is conceivable to reduce the heat dissipation compared to

the currently favored mechanism involving lattice heating. This would represent a significant step towards future energy efficient oxide electronics devices. Ultrafast electron nano-diffraction combined with the required strong (1GV/m and above) THz electric field transients represents the natural tool to investigate the underlying charge-lattice coupling mechanisms. Moreover, electron microscopy on the few nm length and few ps timescales will allow unprecedented insights in dynamical phase separation scenarios [Qazilbash 2007] bringing a large materials class [Imada 1998] within reach of exploration.

Ferroelectrics: Single-cycle THz pulses are of particular interest in providing a unique means of examining the impulsive response of a material to one of the most basic perturbations, that of an applied electric field. Multicycle THz pulses can also serve to resonantly excite the fundamental excitation mode, the electromagnon, of these materials. Ultrafast electron diffraction will allow us unambiguous access to lattice excitations that are coupled to the spin and charge degrees of freedom. This permits exploration of phase changes induced by strong electric fields in ferroelectric and multiferroic materials. Strong (~1GV/m peak electric field) pulses are expected to be able to switch the electrical polarization state in these materials thus also influencing the antiferromagnetic order. In heterostructures, this is expected to be used to switch the ferromagnetic state of adjacent layer offering novel ways to magnetically store information without the need of applying magnetic fields driven by dissipative electrical currents.

Charge Density Wave Systems: In the charge density wave (CDW) state, electrons spontaneously break the crystal translational symmetry by forming a periodic charge density modulation. Such symmetry-broken states can occur due to strong electron-phonon coupling via Fermi surface nesting, or strong electronic correlation. CDW phases have been found in many materials, and are intimately related to a number of important solid state phenomena such as colossal magnetoresistance and superconductivity, and hence can serve as valuable model systems for studying the emergence phenomena with implications far beyond specific materials. For example, the stripe phase in high-Tc cuprate superconductors is conceptually equivalent to a unidirectional CDW, and the prototypical CDW model system TbTe₃ exhibits coupling of superconductivity, charge and magnetic ordering under pressure [Hamlin 2009].

Femtosecond time-resolved diffraction techniques offer exciting new possibilities to study quantum materials in non-equilibrium beyond femtosecond time-resolved x-ray diffraction and complimentary photoemission spectroscopy [Schmitt 2008]. Key is the combination of spatial resolution down to a few nanometers with multi-cycle THz excitation matching and thus resonantly exciting the fundamental CDW excitation modes and strongly coupled optical phonon modes. Thus, studying THz induced CDW dynamics presents a unique opportunity for surgically exciting and ultimately controlling the CDW dynamics on a more elementary level.

High-temperature superconductivity is one of the most intriguing phenomena in solid state physics, and despite intense research for nearly three decades, we are still lacking a microscopic understanding of the underlying mechanisms. Recent experiments on non-superconducting striped, spin- and charge-ordered La_{1.675}Eu_{0.2}Sr_{0.125}CuO₄ suggest that resonant THz excitation of the Cu-O stretch vibration can transiently induce superconductivity by quenching the competing stripe order [Fausti (2011)]. These reports are provocative and have been met with skepticism, yet the idea of using tailored THz excitations

to understand the mechanism of high-T_c superconductivity and ultimately control it are inspiring and present a unique opportunity to transform the field.

Ultrafast electron nano-diffraction, spatially resolving the initial stripe-ordered domains, can provide deep insights into the mechanisms of the lattice response. The question what pathway the phonon system is taking during the transition can be answered by diffraction studies of the lattice response with a time-resolution sufficient to resolve dynamics within the 50fs cycle of the driving THz field. Conversely, it remains mysterious how a coherent, superconducting state on the nanometer length scale, involving many unit cells, could be formed on time scales <10ps. Moreover, the relation of the stripe phase to superconductivity in general is poorly understood and diffraction experiments of the response of the charge ordered state after THz excitation are a critical complement for the discussion of light-induced superconductivity in materials with intertwined ordering phenomena.

Why ultrafast electron pulses?

While ultrafast electron diffraction in combination with optical excitation has been demonstrated, the use of THz pulses will be novel. Current laser-based THz pulses cannot easily access the 3-15 THz frequency range and the peak electric fields of single cycle pulses of sub-ps duration cannot achieve the ~1GV/m values required to drive the whole material into novel transient states. The use of linac-based THz sources will represent a game changer here as the required THz pump parameters are within reach for accelerator sources. The development of ultrafast electron nano-diffraction (~10nm spot size) and microscopy will represent another paradigm change as it opens up complementary measurements of charge/spin dynamics on the same samples as measured at LCLS using soft x-ray holography [Wang 2013] or scattering [Graves 2013].

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2. Understanding Non-Born-Oppenheimer dynamics in molecules

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Summary: We propose the combined determination of nuclear trajectories from ultrafast electron diffraction with electronic dynamics gained from ultrafast soft x-ray spectroscopy to obtain a near to complete picture of the molecular phase space upon photoexcitation. Together with high level *ab-initio* calculations, which are feasible for small isolated molecules, our understanding of the Non-Born-Oppenheimer electron-nuclear coupling can advance to better understand the molecular energy conversion process.

Scientific background: Reactions triggered by optical photons from the sun power nearly all biological functions, either directly or indirectly. Many molecules have the ability to selectively and efficiently convert sunlight into other forms of energy like heat and electric current, or store it in altered chemical bonds. Since the light is not selective concerning the energy conversion, the molecule must provide this property. The photoabsorption results in excited valence electrons. The changed forces between the nuclei result in a highly coupled ultrafast dynamics of nuclei and valence electrons in which the initial photon energy becomes transferred into other energetic degrees of freedom. The efficiency of a particular process depends on its speed compared to the rates of all available processes. For example, the retinals in our eye transform light energy into a special geometry change (isomerization). This is accomplished because the speed of isomerization is faster than the speed for heat creation of that molecule and its environment.

Fig. 4: Conical intersection geometry for the ethylene molecule. Two electronic surfaces calculated using the BOA meet in a cone when plotted as a function of the g and h nuclear coordinates shown on the right. With close proximity of the electronic energies, the BOA breaks down and the molecular wavepacket on the upper electronic state switches to the lower electronic state within femtoseconds (adapted from [Ben-Nun_2000]).

From our current point of view, the fastest, and therefore determining processes in energy conversion, cannot be described with the help of the Born-Oppenheimer approximation (BOA) [Koeppel_2011, Yarkony_1996]. The BOA allows the separation of electronic and nuclear degrees of freedom and is an important tool for the prediction of molecular properties. The breakdown of the BOA allows for coupling between separate adiabatic electronic states, as shown in Fig. 2. The two adiabatic surfaces meet in a cone

when plotting electronic energy as a function of two special nuclear coordinates (g and h), thus the name “conical intersection” (CI) for this special geometry. As the molecular wavepacket on the upper surface (blue) moves close to the point of degeneracy, the energy difference between the electronic states decreases resulting in a very fast transfer from one to the other electronic state (red wavepacket). This mechanism is used by isomerization reactions of retinals in our eye, bacterial photosynthesis, and also the photoprotection of nucleobases inside DNA.

Why ultrafast electron pulses? The approach to understanding the molecular dynamics at CIs is based on a very close interplay of experiments with theory. For photoexcited electronic states, both electron correlation and the correct dynamical propagation play a crucial role and still render calculations extremely challenging [Plasser_2012, Tully_2012]. Experiments to benchmark the simulations need to be performed on isolated molecules matching the single molecule simulations performed on the highest possible level. With ultrafast soft x-rays of LCLS we have an exquisite tool to study the molecular electronic state occupation as a function of time. In the context of Fig. 2 this corresponds to knowing if we are on the upper or lower electronic state. However, we have no knowledge on the nuclear coordinate space, and thus cannot characterize the CI. As shown in Fig. 2, the nuclear motions spanning the CI are complex and we require a high sensitivity tool applicable for dilute targets.

Ultrafast (and elastic) electron diffraction (UED) in small molecules provides a new opportunity to exclusively distinguish the nuclear rearrangements upon photoexcitation. MeV electrons show negligible interaction with valence electrons. The relativistic electrons travel through the scattering medium with about the same speed as the optical excitation pulse, which improves the time resolution compared to keV electron scattering experiments. The direct inversion of the scattering patterns for small molecules is possible, and the method delivers highly accurate nuclear trajectories on the femtosecond time scale. The cross section of elastic electrons at MeV energies is around 0.1 Mbarn [Mayol 1997] and thus about 5 orders of magnitude larger than hard x-ray cross sections, which is absolutely crucial for dilute molecular targets. Expecting about 10^{10} electrons per pulse, the total amount of scattered electrons is about 1000 times higher than at LCLS with 10^{12} photons per pulse. In addition to that, the theoretical structural resolution of relativistic electrons is much higher compared to $\sim 1\text{\AA}$ x-rays at the LCLS. The ultrafast electron diffraction for nuclear geometry determination is thus an ideal complementary tool for soft x-ray electronic state spectroscopy at the LCLS.

The expected bond length change upon optical excitation of small molecules covers a large range. A dissociation reaction, which can be induced in almost all molecular systems, given the right excitation energy, stretches the bond to its breakage. In nucleobases, which are important for our understanding of life’s photoprotection, calculations predict bond changes up to 15% upon photoexcitation. Enhancing the sensitivity to small bond changes will be the main challenge in this task.

A key method to aid the interpretation of the scattering image is the coherent manipulation of the molecular rotational degrees of freedom [Hensley_2013]. Strong femto- to nanosecond nonresonant laser pulses as well as intense THz fields have proven potential to fix several molecular axes in space and even orient the molecule. Moreover, the optical transition to excited electronic states provides selection rules that help in identifying small bond length change.

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3. Matter far from equilibrium: Warm dense matter

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Summary: We propose to use ultrafast electron diffraction to characterize matter far from equilibrium as atomic order is lost and reacquired during interaction of matter with intense, e.g. XFEL radiation.

Fig. 5. View inside the density-functional-theory simulation showing the transition of a solid aluminum lattice into warm dense matter (red particles). Here, the densities are close to solid density of 1.8 g/cc with a temperature of 20,000 K where the interaction potential energy is of order of the kinetic energy resulting in enhanced conductivity. The material properties can be accessed by measurements of the electron-ion equilibration rates with simultaneous UED and optical reflectivity. This scheme holds potentials for discoveries of new material

Scientific background: Warm dense matter is a fundamental state of matter that every material goes through when it interacts with intense ultrafast bursts of radiation. With the advent of powerful x-ray and optical lasers, such systems have received wide attention because of their importance for technical applications and for our understanding of the fundamental physics properties of matter far from equilibrium. For example, laser-driven electron and proton accelerator research has now reached the regime of interest for ultrafast x-ray and beam sources for cancer therapies. To further optimize the x-ray and particle yields theory and modeling plays an important role; yet, they require calculations of warm dense matter conditions that are fundamentally very challenging. This is due to the fact that particle kinetic energies are of the same order as the potential energies allowing no simplifying approximations common in solid state or plasma physics.

Why ultrafast electron pulses? Ultrafast Electron Diffraction (UED) offers a new precision tool to measure the lattice response under intense irradiation. This technique provides time resolution of ~ 100 fs and below. It is a new method for determining the electron-ion equilibration rates that yield the physical properties of warm dense matter. Our experiments will thus be aimed towards simultaneously measuring the optical response of the electron heating by intense photon or particle irradiation and the lattice response as a result of electron-ion interactions. For this purpose, the combination of UED with intense x-ray pump pulses from LCLS will be of great benefit for creating warm dense matter with x-ray lasers. In addition, the recent developments of high-power lasers will further provide the capability for studies of shock-heated systems where energy is first deposited into the lattice with subsequent heating of electrons.

4. Nanoscale materials science

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Summary: Materials Science solutions to the energy problems of modern society require our ability to understand and control the physical processes behind energy conversion, dissipation and storage at the level of the fundamental constituents. Ultrafast x-ray and electron probes that can access the fundamental timescales of these processes with atomic-scale resolution will enable us to master energy and information at the nanoscale. The transformative knowledge gained by these sources will enable a more efficient, top-down design and synthesis of revolutionary new forms of matter with tailored properties, with the ultimate goal to create new technologies with capabilities rivaling those of living things.

Fig. 6: Understanding and managing heat conduction at the nanoscale will enable transformative new technologies such as ultra-efficient microelectronics (left), nanowires with tailored thermal conductivity for thermoelectric applications (middle), and more efficient materials for energy conversion (right).

Non-equilibrium nanoscale phonon dynamics: The problem of heat conduction at nanoscale dimensions¹ is of wide fundamental interest and sets stringent physical limits to the current trend of shrinking micro-electronic devices (see Fig. 4). At nanometer length-scales comparable with the phonon mean free path, conventional heat diffusion based on Fourier's law does not hold and ballistic conduction becomes an important mechanism for phonon transport.² Broad science challenges include the development of an understanding of the dynamics of energy dissipation in nanoscale materials as well as accessing the crossover between the ballistic and diffusive regime of heat and charge transport in nanoscale materials. Fundamental understanding of these phenomena could enable a top-down approach for designing materials for energy applications. However, progress is limited by the lack of local probes of the transport dynamics at the nanoscale across all phonon wavelengths with subpicosecond resolution. Because of the large electron scattering cross section, electron micro-diffraction and microscopy appear as ideally suited probes of these small scales and are complementary to ultrafast x-ray scattering at novel FEL sources. On the other hand, conventional ultrafast electron sources with keV energies suffer from space-charge issues that limit the time resolution and reduced time-resolution due to the temporal walk-off of the optical and electron pulses. There is a clear opportunity for a high-energy, ultrafast, electron source that will reduce these effects. Furthermore the higher energy yields access to larger sections of the material momentum-space accessing Brillouin zones at the same time. SLAC is uniquely positioned for

tackling such challenge with its broad expertise in accelerator development, ultrafast science and materials science.

2D chalcogenides. Transition metal dichalcogenides (TMDC) are a class of materials characterized by van der Waals bonded sheets of trigonal-prismatically coordinated crystals of the chemical formula MX_2 , where M is a transition metal (*e.g.* Mo, W) and X is a Group VI atom (*e.g.* S, Se, Te). In addition to the phonon transport studies mentioned above, monolayer sheets of these materials exhibit several emergent effects (*e.g.* optical second harmonic generation^{3,4}, piezoelectricity⁵) that arise from the lack of inversion symmetry in two-dimensional sheets (space group D_{3h}) with important applications as nanoelectromechanical devices. These effects disappear in bulk and even-layered samples as TMDCs become centrosymmetric (space group D_{6h}) in this regime. In contrast to graphene-like systems, multiple structural phases exist in the bulk and in the single layer limit these distinct phases may play an important role in catalysis for hydrogen evolution^{6,7} and next generation electronic devices⁸. The dynamical structural and electronic processes that occur in 2D materials and how these differ from the bulk response have not been explored. By coupling intense light pulses or ultrafast stresses to these systems, one can trigger large mechanical strains, which have been predicted to undergo a structural phase change from a trigonal-prismatically coordinated (semiconducting) state to an octahedrally coordinated (metallic) one at strains on the order of a few percent⁹. In these systems, coherent interfaces between different phases within a single layer can be formed, giving rise, for example, to metal-insulator junctions within the film, but an understanding of phonon transport across these interfaces, and the unique functional properties that can emerge from these nanoscale structures remains to be understood. Initial studies can be carried out using ~ 10 nm focused electron beams in diffraction mode in order to resolve the nanoscale heterogeneities in these systems. There is a clear case here for pushing the spatial resolution for these studies down to the sub-nanometer resolution in order to visualize directly the atomic-scale structural response of these systems.

Martensitic transformations: Martensitic phase transformations are diffusionless transformations involving small amplitude, coordinated structural reorganizations^{10,11}. They are central to many naturally occurring phenomena including compression during tectonic motion and the release of DNA from viral capsids into host cells and have been utilized in technological applications ranging from the traditional practice of quenching and tempering steel to modern work on shape memory alloys (*e.g.* nitinol) where reversible transformations between related crystal structures enable a range of biomedical applications. One of the outstanding challenges in the study of this type of phase transition has been an understanding of the microscopic transformation pathways by which they are defined, with the first steps occurring on ultrafast time-scales and atomic length-scales in a cooperative fashion. At the nanoscale these processes are expected to be governed by speed-of-sound-like propagation indicating few picosecond time-scales for switching to occur. On the one hand, there is the change in shape of the lattice, and on the other atomic "shuffles" to their new positions are required. The sequence of these events has never been able to be studied before, but will be accessible to the proposed UED/UEM capability. By combining a UEM source running in both imaging and diffraction mode, a fundamental understanding and mapping of these atomistic pathways can be elucidated for the first time. Advancements in the imaging resolution towards

1 nm would resolve the fundamental atomic displacements and pathways associated with these processes, and enable a feed-back-determined optimization and synthesis of new functional materials.

Other systems: Additional opportunities exist with respect to a variety of other important problems in materials science, and have been proposed for this source. Examples include ferroelectric switching dynamics, ion-induced intercalation dynamics at electrochemical interfaces, in-situ growth monitoring of oxygen evolution reaction catalysts by atomic layer deposition, and laser-driven delamination processes for the synthesis of free-standing epitaxial thin films.

Why ultrafast electron pulses?

The key advantage afforded by ultrafast electron pulses for the study of nanoscale materials is the combination of real-space imaging with time resolution - the base capability that would be provided by this source, with of order 10 picosecond time resolution and 10 nm spatial resolution would open up very new possibilities for imaging phonon transport at the nanoscale and single shot nanoscale nucleation events associated with phase transitions. At higher spatial resolution, the impact would be even greater, essentially opening up new means of visualizing not just the structure but the functionality and dynamical processes that underlie nanoscale materials transformations.

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5. Towards sub-nanometer imaging of biological processes

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Scientific background: Proteins and other macromolecules carry out their functions in cells by converting the energy of ligand binding, light or mechanical force into changes in the structure of the protein, which results in altered biochemical properties. For example, hormones and neurotransmitters work by binding to receptors embedded in the membranes of cells; this stabilizes a new conformation of the protein that allows it to bind to and catalyze chemical transformations inside of the cell that are the ultimate result of hormone signaling. Another example is the translation of the genetic code into protein. DNA is transcribed into RNA by a large multiprotein assembly or “machine”, RNA polymerase, which moves along DNA and synthesizes the RNA message. The message is translated into proteins by the ribosome, a large protein-RNA assembly. In both cases, large conformational changes occur at each step in the synthesis of the product RNA or protein. Understanding these processes at a molecular level requires elucidation of the 3D structures of these machines and how they change conformation.

Electron microscopy (EM) and electron diffraction (ED) are key methods to study these structural transformations. EM can provide structures to near-3Å resolution of large macromolecules and their complexes, typically >200 KDa. The most generally applicable EM method is single particle averaging, in which samples are frozen in vitreous ice and imaged. Individual images of randomly oriented molecules are identified, classified according to their orientation, averaged and then used to reconstruct a 3D image. A related method is tomography, where a single sample (large protein assembly, organelle or cell) is imaged at successive tilt angles, and the images reconstructed into a 3D structure. The ability to focus scattered electrons into an image, which is not possible with x-rays, enables direct imaging of molecules. By preparing assemblies in a defined biochemical states, different conformations of the proteins can be determined. Although x-ray crystallography can sometimes be used for this purpose, many large assemblies have regions of high mobility that prevent crystallization. Because EM images single molecules without the constraints of a crystal lattice, it is very often the only way to obtain direct structural information at the molecular level.

Membrane proteins represent approximately 30% of all proteins in the cell. They are critical for cell-cell communication and signaling, and energy transduction in metabolic pathways and photosynthesis. Because they are embedded in a lipid environment, membrane proteins are very challenging to purify and to crystallize. However, some membrane proteins can be coaxed to form 2D crystals, which are crystalline in the plane of the membrane but not normal to the plane. Diffraction from such crystals has been used to solve the 3D structures of several membrane proteins. A series of diffraction patterns is typically measured from a single 2D crystal by tilting it with respect to the beam. Given the much stronger scattering cross-section of electrons versus x-rays, ED has been the method of choice for 2D crystallography. Very recently, it has been shown that electron diffraction can be recorded from very small 3D crystals (< 500 nm) and used to determine structures. Since very small crystals can have better

intrinsic order due to fewer growth defects, this method is an attractive potential alternative to traditional 3D x-ray crystallography.

Why ultrafast electron pulses? Beam-induced damage limits resolution in both biological EM and ED. The proposed instrument has the potential to overcome this problem for ED by enabling measurement of data in the fs regime, which is likely faster than beam-induced damage, analogous to the “diffract-before-destroy” method in use at the LCLS for x-ray crystallography. Again, the stronger scattering of electrons versus x-rays should provide a decisive advantage for damage-free 2D crystallography. Although 2D-ED has relied on tilting of a single sample, single shots using multiple 2D crystals could be employed. It has already been demonstrated that diffraction from small 3D crystals randomly oriented on a standard sample grid can be recorded, integrated and scaled to produce a data set. The ability to measure damage-free data from small 3D crystals could provide an important alternative to LCLS, which has limited capacity.

A potentially transformative application would be to examine time-resolved structural changes by UEM. Many of the important conformational changes that occur in proteins happen in μs – ms (or longer) time scales, and cannot be studied in crystals as movements of protein domains typically destroys the crystal, limiting time-resolved diffraction studies. This application represents a key advantage for electrons: although time resolved SAXS is possible, it has a far lower information content than directly imaging the molecules, since modeling the scattering object from SAXS data is a fundamentally underdetermined problem. Free of crystal lattice constraints, *the new UEM instrument would allow for the first time direct imaging of biologically important conformational transitions of macromolecules and their assemblies in real time*, which at present can only be inferred from indirect spectroscopic or scattering methods.

We envision that a solution of the macromolecule or macromolecular assembly would be delivered in a thinly focused liquid jet, after triggering a reaction by standard rapid mixing or optical pumping methods. Given the flow rate, snapshots of collections of molecules at a given time, in the μs – ms range, after the start of the reaction would be recorded. Although this will be an ensemble with some distribution, modern image processing programs can sub-classify heterogeneous conformations. A liquid jet delivery system has already been described in the literature, and the order of magnitude higher energy of the instrument would allow the use of relatively large diameter jets (several hundred nm) that would still be in the focal plane of the instrument. Also, many cryo-preserved biological molecules are damaged by surface tension of the thin layer of vitreous ice in which they are embedded, so the jet delivery would alleviate this problem. The absence of ice would provide lower background, improving signal-to-noise.

To achieve this goal, the instrument will require a focal spot on the order of $1\ \mu\text{m}$, and transverse and longitudinal coherence lengths of 1-10 nm and ~ 50 nm. These parameters will require longer pulse times (ps range), so damage-free imaging will probably not be possible. However, from an imaging perspective this experiment is equivalent to the low-dose imaging regime in routine use for cryo-preserved specimens. As long as the pulse is faster than the tumbling time of the molecule (typically ns time scales), an unblurred image can be obtained. Moreover, it is well known that many samples are damaged by surface

tension of the thin layer of vitreous ice, so the jet delivery would alleviate this problem, and the absence of ice would provide lower background, improving signal-to-noise.

Fig. 7: Schematics of the setup for time-resolved imaging of biological processes.

6. Understanding nanoscale spatio-temporal correlations of glasses

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Scientific background: Although periodic and symmetric objects are favored by human beings, the fact is that the most matter in the universe is in the state of glass, which is random and disordered. Understanding the structure and dynamics of disordered glasses has been one of the most challenging scientific issues of today. Different from crystals that experience a first-order transition from liquid to solid, the transition from liquid to glass is a continuous “frozen” process when a liquid is cooled sufficiently fast to a supercooled liquid state and crystallization is avoided. This falling out of thermodynamic equilibrium occurs across a narrow transformation range where the characteristic molecular/atomic relaxation time increases abruptly (but continuously) from a few picoseconds to the order of seconds with respect to temperature decrease. The underlying mechanisms of the dynamic arrest of supercooled liquids, i.e. glass transition, are still in debate despite great efforts devoted to this problem for over half a century [Kauzmann 1948, Debenedetti 2001]. This is mainly due to the lack of experimental observations on the local structure evolution in supercooled liquids and glasses with both high spatial and temporal resolutions.

Fig. 8: Example of static nano-beam diffraction from a $\text{Zr}_{66}\text{Ni}_{33}$ metallic glass (from [Hirata 2011])

Why ultrafast electron pulses? The achievable spatial resolution is mainly limited by the nonexistence of long-range translational and rotational symmetry in glasses and supercooled liquids, which renders it experimentally inaccessible to determine their local atomic/molecular structure by conventional diffraction/imaging methods. We recently developed an angstrom-beam electron diffraction method to probe local atomic configurations of amorphous matter by utilizing ~ 0.4 -1 nm coherent electron beams. We experimentally revealed the pronounced local atomic order in the length scale of 1-2

nm in disordered glasses (Hirata 2011) as reproduced in Fig 6. We also provided compelling evidence that geometric frustration of the local order is the origins leading to the transition from local order to long-range disorder [Hirata 2013]. The static structure characterization has a strong indication that the glass transition is associated with the development of strong inter-atomic/inter-molecular correlation of constituent atoms/molecules in supercooled liquids during cooling. However, the dynamic process of the transition from supercooled liquid to glass has not been experimentally explored. The crucial step to solve this issue is to develop a powerful experimental tool that is capable of detecting nanoscale (1-2 nm) local structure of supercooled liquids and glasses at the time scale of 1-1000 picoseconds. The recently-emerging ultrafast MeV electron diffraction/imaging is probably the only technique that is capable of achieving this goal. This speculation is based on the known advantages of this technique: i) the electron has a large scattering cross section for strong diffraction from small objects; ii) the electron beam can be focused by electromagnetic fields to reach 1-2 nm spatial resolution; iii) an MeV electron with a short wavelength can provide high-Q scattering for detailed local atomic/molecular structure; and iv) the time resolution is better than 100 fs.

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