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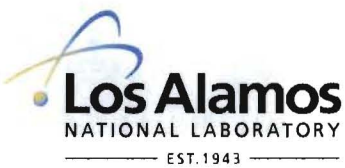

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MaRIE Theory, Modeling and Computation Roadmap
Executive Summary

Context

The confluence of MaRIE and extreme (exascale) computing timelines offers a unique opportunity in co-designing the elements of materials discovery, with theory and high performance computing, itself co-designed by constrained optimization of hardware and software, and experiments. MaRIE's theory, modeling, and computation (TMC) roadmap efforts have paralleled "MaRIE First Experiments" science activities in the areas of materials dynamics, irradiated materials and complex functional materials in extreme conditions. The documents that follow this executive summary describe in detail for each of these areas the current state of the art, the gaps that exist and the roadmap to MaRIE and beyond. Here we integrate the various elements to articulate an overarching theme related to the role and consequences of heterogeneities which manifest as competing states in a complex energy landscape. MaRIE experiments will locate, measure and follow the dynamical evolution of these heterogeneities. Our TMC vision spans the various pillar science and highlights the key theoretical and experimental challenges. We also present a theory, modeling and computation roadmap of the path to and *beyond* MaRIE in each of the science areas.

Heterogeneities and the Mesoscale

The last 50 years have seen enormous progress in our understanding and control of single crystal or homogeneous systems. Similarly, we have developed numerous tools to describe equilibrium properties, both thermal and dynamic equilibrium. Perturbation about the bulk, periodic or translationally invariant equilibrium state has given rise to the notions of phonons, magnons and other excitations. However, it has become increasingly evident that heterogeneities due to the presence of disorder, defects and interfaces (e.g., concentration of energy in "hot spots" as in HE initiation or adiabatic shear banding in materials that otherwise seem homogeneous) are key to understanding their function and performance. These heterogeneities can be intrinsic to the material as in disordered polymeric systems with heterojunctions at the interface of two dissimilar media or extrinsic, as in the emergent functional phases that arise in correlated electronic systems due to the interplay of spin, charge and lattice. The heterogeneities, typically over nanometers to microns in length scale, can control the behavior of the system by affecting the free energy balance in favor of certain preferred states or outcomes. Adiabatic shear banding can lead to sudden failure; the percolation of local irradiated damage in zircon due to recoil can have a sudden affect on elastic and thermal transport; and a small magnetic field in a perovskite manganite with coexisting insulating and conducting phases can give rise to a hundred fold decrease in resistivity. The preferred state may be considered the result of competition in a complex energy landscape that is a function of the variables spanned or order parameters. The grand challenge opportunity is that the complexity of the landscape can be put to good advantage to control desired performance, rather than be a characteristic which one attempts to avoid.

Several examples of energy landscapes involving competing states, one in equilibrium and the other far from equilibrium, help to illustrate the theme and why landscapes are part of understanding the physics we want to exploit through MaRIE . An outstanding problem in

ferroelectrics is the search for Pb-free piezoelectrics to replace PZT. Recently, the solid solution BZT-50BCT was discovered with a value for the piezoelectric coefficient, d_{33} of 620 pC/N, comparable to that of PZT. Landau theory , at the homogeneous , equilibrium level, provided the key insight into the form of the phase diagram for PZT. The temperature-concentration phase diagram for PZT consists of three first order transition lines that terminate in a second order critical point that is a tricritical triple point. Moreover, by demanding that the morphotropic phase boundary (MPB) between the two polarization distortions, rhombhohedral and tetragonal is vertical, the free energy for the polarization becomes purely isotropic, allowing for a large susceptibility. PZT has almost a vertical MPB with a small barrier to polarization switching. The reason Pb-free ferroelectrics discovered previously were vastly inferior is because the MPB is not vertical and there is no tricritical triple point. The energy barrier to switching is large. Thus, there is nothing special about Pb itself. Real piezoelectrics are heterogeneous and in order to achieve desired performance by domain and interface engineering, it would be necessary to exploit the complex energy landscape. This is precisely the kind of effort envisaged in MaRIE's Making, Measuring and Modeling Materials Facility (M4).

The importance of rate dependence and departures away from equilibrium in exploiting the energy landscape is highlighted by the deformation characteristics of nanowires. Surface effects activate physics that is not as easy to probe in the bulk; however, it illustrates the need for similar measurements on mesoscopic and bulk systems. Stretching a nanowire induces complex changes in the energy landscape. High strain rates do not allow the system to easily sample phase space and the system gets stuck in local energy minima. In this case the pathways which are favored are those that lead to accumulation of defects such as stacking faults resulting in necking and failure. On the other hand stretching at low strain rates allows these stacking faults to anneal by creation and annihilation of defects and the system is able to probe other regions of stability in the energy landscape, such as phase transformations (FCC to icosahedral at a different width) or other failure modes. A study such as this has only been possible through the development of accelerated molecular dynamics algorithms that can access millisecond time durations. Temporally and spatially resolved in-situ measurements are therefore a key in following the deformation mechanisms. Current TEM methodologies are too slow to capture these unit processes. Rather, what's required are analogous in-situ time and space resolved deformation studies on mesoscopic wires (with several to many grains) and bulk samples using x-ray scattering techniques (e.g., at MaRIE's Multi-Probe Diagnostic Hall).

We thus need to consider perturbations about an intrinsically heterogeneous state to describe excitations that are the analogs of phonons and magnons --- i.e., how do we go beyond the "Bloch paradigm"? Similarly, in order to describe driven systems which may have disparate time scales, we need to go beyond thermal equilibrium or the Maxwell-Boltzmann distribution. The notion of an effective temperature that is related to the configurational entropy associated with stirring a system, but is different from thermal temperature, may be an appropriate state variable to describe nonequlibrium systems, especially at low temperatures where thermal fluctuations are weak. We have only recently begun to address this question and explore its implications for materials. Similarly, departure from a one-particle distribution that obeys the Boltzmann equation to a correlated multiparticle distribution is a path towards describing departures away from equilibrium. However, if the temporal heterogeneity or extreme conditions are such that the time

scales of the drive (e.g., from a shock), are of the same order of magnitude as the temporal fluctuations in the system, then this is an even more challenging problem. The spatial and temporal scales are in general coupled and a key issue is to understand and exploit this coupling. Hence, the central theoretical and experimental challenge for MaRIE and the beyond is how to "go beyond both Bloch and Boltzmann." Currently, we are beginning to develop rudimentary tools to address the first aspect, independent of the second, for which we have just barely scratched the surface.

Extreme environments such as those realized at MaRIE's Fission-Fusion Materials Facility (F^3) force systems to be intrinsically far from equilibrium and this has ramifications for MaRIE experiments. In equilibrium systems, the machinery of thermodynamics and statistical mechanics can be applied to predict transitions such as solid to liquid or magnetic to nonmagnetic. The equilibrium phases have no time dependent behavior since the system is assumed to have fully equilibrated before any measurements are taken. For example, the onset of a phase transition may be dramatically altered, the transition might be prevented from occurring, or entirely new transitions may appear in the nonequilibrium state. Other properties of the system, such as elastic constants, conductivity, viscosity, or other structural aspects, may significantly change from their equilibrium values.

One of the most active areas of physics in recent years has been the development of nonequilibrium statistical mechanics. New theoretical frameworks have been devised to treat systems in which rare events or extreme statistics play a disproportionately large role in determining the response of the materials. Such systems include earthquake faults, Barkhausen noise in magnets, stock price fluctuations, and fluid turbulence. Materials driven out of equilibrium or subjected to extreme conditions can experience fluctuations that place the sample into a state which resembles neither a solid nor a liquid. Instead of exhibiting the standard Boltzmann or Gaussian fluctuations, the system may undergo fluctuations with highly skewed or nonstationary distributions with heavy tails that make extreme events more likely to occur. Rapid transient behavior may be followed by the development of an extremely long lived metastable response state, making it necessary to quantify how far the system is from equilibrium and how long metastable states can persist. Many of these processes can be modeled using techniques from nonequilibrium statistical mechanics. In some cases, there are well defined transitions among nonequilibrium states that can be described in terms of critical phenomena or absorbing phase transitions. These transitions have universal properties that occur in a wide range of different systems that fall into the same universality class. The materials conditions to be studied in MaRIE will require the extensive use of nonequilibrium statistical mechanics.

It is at the "mesoscale" between nanometers and microns that the collective behavior and self-organization associated with the heterogeneous phenomena discussed above occur. Nucleation, growth and coalescence, be it of voids due to spall or the formation and growth of a critical droplet, occur at this spatial scale. It is arguably the least studied of the relevant length scales. The limiting cases -- the world of the very small or the very fast, and in some cases, both, and that of the very large and slow – we basically know how to treat theoretically. Moreover, existing experimental facilities provide capabilities to make measurements on these scales, especially in the microscopic regime. However, it's the mesoscale where we do not have the theoretical tools

developed or the experimental means to study the collective behavior in bulk samples under extreme conditions. In addition, the mesoscale serves as a "hub" for information to be propagated in both directions, i.e., to larger or smaller length scales. Thus, a perturbation or boundary condition imposed at the macroscale will propagate to lower length scales, and similarly information resident at lower length scales can emerge via the mesoscale. MaRIE's in-situ space and time resolved measurements at the mesoscale will therefore challenge and allow for the development of theory and models to unravel the coupling of spatial and temporal scales.

The happy convergence of MaRIE and extreme (exascale) computing time lines gives us an excellent opportunity to change the way we tightly couple the elements of materials discovery, theory, computation and experiment. Further, it is much easier to develop and implement this integration with a capability that is being planned, rather than 'retrofitting' existing assets with inherent difficulties of bringing the pieces together at scale. Computation includes information science and technology tools that play an important role spanning specific materials phenomena, such as data analysis, microstructural reconstruction, and imaging and image analysis methodologies. Exascale computing would allow us to examine the physics of collective phenomena, such as nucleation, growth and coalescence as well as the effects of poycrystallinity, as they demand relatively large system sizes and long times. Acceleration algorithms currently available access at most several milliseconds for small enough systems or a trillion atoms for a few picoseconds. Similarly, from the continuum end, the solutions of the macroscale equations are only valid to about 150 microns without the need to include additional physics. The intermediate, mesoscale regime is precisely where the challenge of bridging scales exists and where MaRIE experiments are crucial so that in-situ data can be used to bridge atomistic and continuum level simulations.

We now consider each of the science areas that have been under study within this TMC roadmap activity and that are described in detail in the following chapters. We provide here a bird's eye view of the state of the art of theory, the integration with MaRIE First Experiments, and the roadmap to MaRIE and beyond.

Materials Dynamics

A typical experiment in which a material is shocked is accompanied by a range of coupled physical processes. These include phase transformations, damage, plasticity, twinning, adiabatic shear banding and recrystallization. The theoretical challenge is to decouple these processes, understand their relative role and importance, especially under extremes of pressure, temperature, strains and strain rate, and re-integrate that understanding into a self-consistent framework. Currently, our descriptions rely on obtaining constitutive behavior from homogeneous, bulk, equilibrium systems. This effective "mean field" approach is also used for damage as well as multiphase equation of state (EOS) or multiphase strength models. The basis of this approach relies on solving the conservation equations using materials constitutive laws to provide closure, in addition to the evolution equations. Consistent with the theme of an energy landscape, this thermodynamic formalism separates the elastic and inelastic potentials so that, for example, the plastic potential or yield surface has a form where the shape accounts for the influence of

anisotropy or texture and the radius is related to material strength and damage. Small scale experiments over several decades have largely helped to determine the form of these potentials.

In the next 5-10 year period we will increasingly use lower length scale methods to inform and refine these potentials, especially at high strain rates and large pressures. For example, better homogenization schemes for polycrystals that are based on refined single crystal models, which in turn are informed by dislocation dynamics simulations, will lead to better potentials. In addition, our models do not consider shear effects on phase transformations. Only volumetric or uniform pressure effects are incorporated and this is not adequate for describing strategically important materials such as U6%Nb. In addition, phases only transform in the bulk; a computational cell can have either of the phases or a mixture and no interfacial energies are included. Moreover, there are no effects of phase transformation on plasticity or vice-versa. For example, at high pressures in Zr, the plastic strain associated with the transformed phase is not known. At high strain rates shear becomes important in the coalescence of voids. This is not incorporated in our damage models and neither is the coupling of EOS to shear, even to determine if it is significant or not in certain regimes. As these models are mean field, there are no fluctuations or spatial variations in the state variables. In short, our models do not incorporate heterogeneities; however, over the next decade we will see a greater emphasis on filling some of these gaps within the current, established framework to meet certification challenges.

To describe the complexity of the yield surface for inelastic processes that include heterogeneities requires a departure from effective field approaches. The MaRIE and beyond time frame entails lifting these approximations so that the fields describing the key heterogeneous physics are coupled together with appropriate gradients, fluctuations, long-range interactions and memory kernels. Hence, a polycrystal model would make no homogenization assumptions nor enforce ad-hoc conditions at grain boundaries. The potential or macroscale closure relations would arise out of a model which would be informed by lower length scale strategies. With the emergence of exascale computing, we envisage large scale computations of such mesoscale/polycrystal models to approach the macroscale.

Information Science and Technology tools will play a pivotal role in advancing theory. For example, sensitivity analyses will determine important parameters, especially as a tool to bridge different techniques, such as phase field and molecular dynamics. Machine learning tools for microstructure reconstruction will provide insight into the spatial distribution of rare events that could lead to failure. Inversion of data, be it from experiments or simulations, will help to identify structural characteristics associated with fine blurring signatures in scattered patterns. Efficient and stable numerical approaches that can track interfaces and heterogeneities and can avoid instabilities, which are currently hurdles in solving equations, will be required.

MaRIE First experiments on "*Microstructure Based Heterogeneity Evolution Leading to Material Phase Transformation and Damage / Failure Events*" and on *"Influence of Stochastic Explosive Microstructure on Detonation"* will directly provide in-situ data at the scales spanning polycrystal to single crystal behavior to develop models at these lower length scales as well as to parameterize the coupled polycrystal field model. These experiments will study solid-solid

phase transformations, void damage, the role of grain boundaries on strength, as well as the collective behavior associated with hot spots in high-explosive detonation.

Irradiated Materials

The strategy for the development of theory for materials of relevance to nuclear energy is very similar to that for materials dynamics. The key issues for energy applications are an understanding of the fuel's center line thermal transport and the stresses at the fuel-clad interface. Creep is a dominant mechanism and the current state of the art uses a rate dependence obtained from engineering level correlations. The form has minimal content in terms of any damage properties, unlike the plastic potential for materials dynamics. It is independent of burn-up or material history but depends on temperature, neutron flux and Hoop stress at the fuel/clad interface, and material parameters are obtained from experimental data. Thermal transport and evolution equations for species density (vacancies, interstitials, fission gas bubbles) are coupled with this creep evolution together with a strength model for the stress. This is the state of the art that is encoded in FRAPCON [http://www.pnl.gov/frapcon3/] and solved for 1-d radial distributions for different pellet cross-sections.

Developments in the next 5-10 years will include using lower scale techniques, such as single crystal and polycrystal phase field models, kinetic Monte Carlo, molecular dynamics and electronic structure calculations to obtain the various material parameters and performing full 3-d continuum calculations. However, the continuum model will include little, if any, aspects of microstructural effects. Recent simulation studies reveal that interfaces play a key role. The evolution equations for species diffusion could potentially involve sink terms for defects at interfaces to describe radiation tolerant properties.

For MaRIE and beyond, our roadmap calls for a mesoscale/polycrystal model involving coupled fields where, for example, the creep rate is a function of time, burn-up, stress, dislocation density, thermal history as well as the corrosion state. In addition, the thermal conductivity will be dependent on space and time as well as burn up. That is, it will be sensitive to the local microstructure or damage. The MaRIE First Experiment "*Inside a Nuclear Fuel: Measurements of Temperature, Microstructure, and Thermal Transport*" will provide precisely this input. Fission gas release measurements ("*Fission Gas Bubbles and Concomitant Swelling in UO_2 Nuclear Fuel*") will help to establish transport mechanisms and provide mobilities for the species evolution. Similarly, measurements of dislocations interacting with pinning centers in "*In situ Mechanical Testing of Structural Materials in a Fusion/Fission Relevant Spectrum*" will inform strength models for cladding materials. Bridging between methods at the lower length scales is an important ingredient to distilling key variables and obtaining estimates of parameters. As in material dynamics, the macroscale closure relations will manifest from the coupled mesoscale/polycrystal model.

Complex Functional Materials

We have referred to the importance of coupling spin, charge and lattice degrees of freedom and the role of defects, disorder and interfaces in determining functionality. A particular aspect that is relevant to MaRIE's M4 Facility is how to describe, control and engineer these heterogeneities. Understanding nanoscale heterogeneties and nonequilibrium relaxation will require scanning and time-resolved probes at nm-microns length scales and pico- to femto-second time scales. On the 5-10 year horizon, approaches that go beyond Bloch, such as multiple-band electronic structure, Dynamical Mean Field Theory, and spatially local electronic structure calculations will need to be further developed. These will need to capture lateral electronic, magnetic and lattice heterogeneities and use them as inputs into correlated electronic models. Expected model predictions include phase diagrams as functions of competing interactions, strain, doping, temperature and magnetic field dependence. Dynamical approaches beyond Boltzmann using realistic time dependent electronic and lattice states will be a challenge, both theoretically and experimentally, as current time resolved dynamical measurements are analyzed primarily in terms of effective single relaxation times.

Electron-hole separation at hetero-junctions in disordered materials is important for device-scale modeling at the mesoscale. Multiscale modeling calls for determining mobilities from lower length scale master-equation or tight binding approaches, which in turn need electronic structure input. The role of disorder in trapping states and implications on mobilities in materials with bi-continuous interfaces is a challenge. Although methods for handling layered materials where the hetero-junctions are boundary conditions are in their infancy, the ability to handle disordered interfaces in a similar manner is a challenge appropriate for the MaRIE timeline (and the experimental capabilities that will be available).

Summary and Outlook

Theory, modeling and computation must be coupled to MaRIE experiments because they provide the means to develop a consistent framework that integrates different sets of experimental data. Its role is analogous to connecting isolated data points to fill in a portrait. Theory provides the means to explore regimes of parameter space, such as high strain rates or high pressures, that are experimentally not accessible. Finally, TMC provides a predictive capability so that new phenomena that are suggested may be probed by designing new experiments. We envisage an integrated MaRIE capability in which theory, high performance computing and experiment are tightly coupled in real time with feedback for efficient control. An example is the investigation of shock phenomena in a solid. The x-ray diffraction patterns would characterize the average structural behavior. A high performance computer simulation would provide data related to the heterogeneities that will be diagnosed by machine learning tools. The diffraction pattern from the solid may be compared to that of the experiment to help characterize the signatures for the diffusive features in the pattern or provide feedback to experiments regarding change of beam intensity or detector location. The final step is quantitative comparison and coupling of experiment and simulation to theory and feedback to improve theory and drive materials discovery.