I.1 Scientific Overview: The interaction of fluids with solid substrates controls many chemical processes encountered in nature and industry. However, the atomic/nanoscale reactivity, structures and transport properties of the fluid-solid interface (FSI) are poorly understood for the vast majority of fluid and substrate combinations, particularly at environmental extremes (e.g., high surface charge density, extreme chemical non-equilibrium, high ion/electron fluxes, high temperature/pressure). This lack of fundamental molecular-level understanding of interfacial phenomena has often lead to Edisonian approaches to the resolution of technological challenges related to advanced energy technologies, including fuel cells, solar energy utilization, batteries, supercapacitors, corrosion-resistant materials, combustion, heterogeneous catalysis, and chemical separations. This contributes to our inability to tailor interfacial systems efficiently, or to predict performance spanning weeks (catalysts), years (electrical energy storage devices), decades (fossil and nuclear power plants), and millennia (CO_2 sequestration, nuclear waste isolation). To address these challenges, a paradigm shift is needed in our understanding of the FSI, away from continuum solvent descriptions and hypothetical interfacial structures, toward a *quantitative, fully dynamic, and chemically realistic description of the interactions of electrons, atoms and molecules that give rise to macroscopic fluid/solid interfacial properties.*

This Center will bring together a multidisciplinary team of scientists, postdoctoral associates and students to redefine the FSI and enable predictive understanding and control of interfacial processes. The overarching goal of the Fluid Interface Reactions, Structures and Transport (FIRST) Energy Frontier Research Center will be to address the fundamental gaps in our current understanding of interfacial systems and answer these questions of high importance to future energy technologies:

- *How does the interfacial region differ in structure, dynamics and reactivity from the bulk properties of the fluid and solid phases?*
- *How do these altered properties couple with complex interfacial textures to influence chemical reactions, ionic and molecular transport and charge transfer within and across the interface?*
- *How can we control and manipulate interfacial phenomena by informed selection of fluid- and solid-phase components, interfacial geometries, field gradients, temperature, pressure and other environmental parameters?*

These questions permeate the fundamental science needed to solve our nation's long-term energy production, storage and utilization needs, as described in nearly all of the DOE/BES Basic Research Needs and Grand Challenge reports (**Table I.1**). The FIRST Center will focus mainly on FSI systems of relevance to electrical energy storage and catalysis for energy applications. The research will be pursued in three parallel thrusts that address increasing levels of FSI complexity, ranging from the alteration of the bulk fluid and solid properties due simply to their juxtaposition at a planar interface (Thrust 1), to the effects of surface roughness, porosity, functionalization and reactions between the fluid and substrate on the FSI properties (Thrust 2), to surface reactions that are mediated by the interfacial fluid (Thrust 3).

The unique properties of FSI systems emerge from a complex interplay of short- and long-range forces and reactions among the molecular fluid components, solutes and substrates. Potential gradients (chemical, electrical, etc.) can be highly non-linear at the angstrom-nanometer scale. The finite size, shape, directional bonding, charge distribution and polarizability of solvent and solute fluid components are convoluted with their ability to reorient, 'unmix' and react with one another and the substrate. The truncated solid surface exposes under-bonded atoms that drive dynamic interactions with the adjacent fluid by local bond relaxation,

charge redistribution, dissolution, precipitation, sorption and porosity development/destruction. **Figure I.1** shows the commonly-invoked, but century-old, Gouy-Chapman-Stern-Helmholtz concept of the electrical double layer (EDL) at the interface between a negatively-charged metal oxide surface and an aqueous electrolyte solution. We intend to replace such static, hypothetical, continuum models with what we will refer to as "FSI models" that capture the atomic-molecula-nanoscale structural, reactive and transport properties of real interfaces, over the relevant time (femtosecond-millisecond) and length (sub-angstrom to sub-micron) scales of interfacial systems. *This will provide an unprecedented level of understanding, predictability and control of interfacial transport and reactivity, and provide guidance for the design of new materials with extraordinary properties to address our future energy needs.*

However, there are barriers to achieving predictive understanding of FSIs, including: (a) failure at the molecular scale of macroscopic continuum theories for interaction of matter and energy; (b) thermodynamic descriptions of chemical equilibria and reaction kinetics that are species-nonspecific; (c) nanoscale dimensionality of the interface itself; (d) highly-divergent structural and dynamic properties of the juxtaposed phases which permits non-equilibrium conditions to persist; (e) very localized and large variations in phase composition, dynamics, chemical and electrical potential on both sides of the interface; and (f) extremes of pressure, temperature, reactivity, field gradient and other harsh environmental conditions relevant to many energy technologies. Even for FSIs that have been extensively studied at the molecular level in recent years (e.g, aqueous electrolytes at metal and metal oxide surfaces, **Fig I.1**) there have been very few integrated efforts that combine the most advanced computational approaches with detailed structural and dynamic probes to produce models with truly predictive capability.

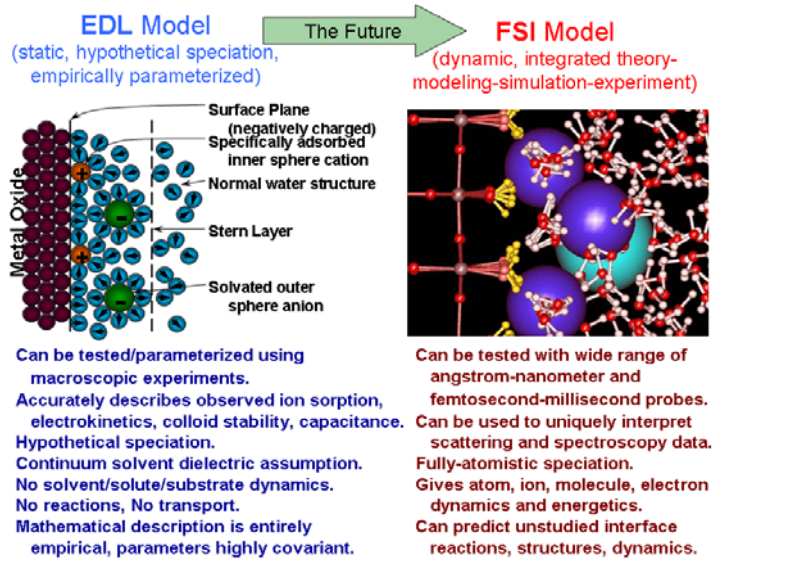

Figure I.1. Gouy-Chapman-Stern-Helmholtz model of the EDL at a negatively charged metal oxide surface in contact with an aqueous RbCl solution, compared with the fluid-solid interface (FSI) model promoted in this proposal. In this case, the FSI model is based on a CMD simulation that was developed and tested using static and dynamic *ab initio*, synchrotron X-ray and neutron scattering, and macroscopic titration and electrokinetic approaches (Bandura, 2004, 2008; Předota, 2004a,b, 2007; Zhang, 2004, 2006a,b, 2007; Wesolowski, 2008; Machesky, 2008).

Our strategy to overcoming these barriers is to take a hierarchical and highly-integrated approach, coupling unique experimental, chemical imaging and computational probes of FSI structures, reactions, and transport phenomena. The effort will be divided into three synergistic thrusts, illustrated in **Figure I.2.** The thrusts address increasing levels of FSI complexity while

providing feedback that will enhance the outcome of each thrust, such that the overall effort greatly exceeds the sum of the individual parts.

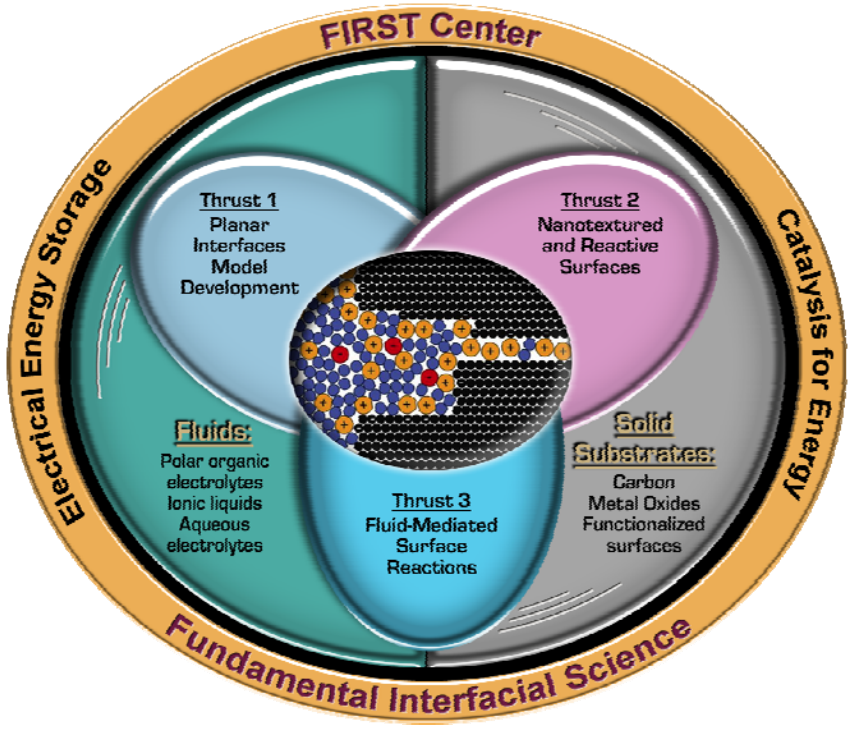

Figure I.2 FIRST Center concept, showing linkage among the three thrusts, the focus of each thrust, the solid and fluid phases to be investigated, and the primary energy technology application areas that will ultimately benefit from the proposed research. The insert is a hypothetical schematic of a nanoporous carbon electrode supercapacitor (Electrical Energy Storage workshop report, Fig. 13, see **Table I.1**).

Table I.1. Fluid-solid interfacial phenomena impact advanced energy technologies identified in DOE BES Basic Research Needs and Grand Challenges workshop reports (http://www.sc.doe.gov/bes/reports/list.html).

Basic Research Needs Workshop Reports:	Energy Applications	FIRST Thrust			
		1	2	3	4
Advanced Nuclear Energy Systems	Separations, reprocessing	x			x
Catalysis for Energy	Heterogeneous catalysis	x	x	x	x
Clean and Efficient Combustion	Mixed fluids at surfaces, corrosion	x			x
Electrical Energy Storage	Supercapacitors, batteries	x	x	x	x
Geosciences	CO_2 sequestration, waste isolation	x	x		x
Hydrogen Economy	Gas storage, fuel cells	x	x	x	x
Materials under Extreme Environments	Metals corrosion, solid oxide fuel cells	x	x		x
Solar Energy Utilization	Photocatalysis, biofuels conversion	x	x	x	
Grand Challenges:					
Chap. 2. Basic Architecture of Matter	Catalysis, Fuel Cells, Materials Synthesis	x	x	x	x
Chap. 6. Matter Far Beyond Equilibrium	Catalysis, Materials stability, 'Jamming'		x	x	x
Chap. 7. The People and Tools Required	Interdependent Science	x	x	x	x

In Thrust 1, we will investigate fluid (aqueous, polar organic, ionic liquid) interactions with charged and uncharged 'solvophobic' (carbon) surfaces in a planar or unconfined geometry.

This will enable the application of advanced neutron, X-ray, NMR and nonlinear optical probes of interfacial structure and dynamics and facilitate coupling these atomic-nanoscale imaging results with multiscale computational models that capture the chemical realism of FSIs that will be studied in the other Thrusts. In Thrust 2, we will investigate how nanoscale confinement and surface functionalization influence solvent/solute transport at tailored carbon and metal oxide surfaces with unique control of interfacial geometry and electrolyte chemistry and structure. We will also investigate the effect of surface chemical and textural evolution through time, such as is encountered during "Solid-Electrolyte Interphase" (SEI) foromation at battery electrode surfaces. In Thrust 3, we will determine how the unique properities of interfacial fluids couple with reactive surface sites to control reaction pathways, selectivity, and energetics. We will focus on proton-coupled electron transfer reactions in the electrocatalytic reduction of CO_2 and O_2 in water and dense gases. These thrusts will be pursued in parallel, but will involve intensive integration of effort and involvement of the same team members across the thrusts. The goal of these thrusts is to develop FSI models that capture the actual structural, compositional and electron-atom-molecule interactions that control interfacial properties, reactivity and transport. The level of computational rigor and molecular-level detail incorporated into the FSI models will vary from one thrust to another, as the FSIs increase in complexity. These models will also evolve through integration among the thrusts, and breakthroughs in computational and experimental capabilities in this program and throughout the scientific community. We fully intend to modify our targets and approaches judiciously, as these new opportunities arise. An intensive effort to share our results with the broader scientific community and engage experts across the energy technology landscape will keep the FIRST Center at the forefront of interfacial science and offer a rich environment to train the next generation of scientists to meet 21st Century energy challenges.

I.2 Management Plan: This research program is anchored in ORNL's core strengths in chemical, materials, neutron, computational, and nanoscale sciences, which will ensure scientific excellence. The Center's partner institutions complement and extend the scientific expertise and will enhance educational outreach. As DOE's largest multi-purpose science and energy laboratory, ORNL has deep experience in leading multidisciplinary projects of this magnitude and complexity, from basic science through technology development to industrial applications.

Organizational Structure, Roles, and Responsibilities: The FIRST Center management structure, outlined in **Figure I.3**, has been designed to accomplish the scientific goals of the Center, while providing synergy between the thrusts, educational outreach, oversight, and operational support. The **Director** is responsible for the overall scientific direction and management of the Center, including setting scientific priorities, monitoring progress, allocating resources, and ensuring compliance with environmental, health and safety regulations. The Director is accountable to the Associate Laboratory Director (ALD) for Physical Sciences and BES Program Managers. The **Thrust Leaders** report to the Director and will be responsible for managing the daily activities of their specific thrust, which includes setting scientific priorities, monitoring progress and managing resources. The **Steering Committee** (SC) will coordinate activities across the four thrusts, and the **Cross-Cut Team** (CCT) will be responsible for integrating and coordinating common experimental and computational techniques across all four thrusts. The **Internal Advisory Board** (IAB) will provide oversight on project goals and priorities and links to BES Program Managers, ORNL programmatic research, and ORNL User Facilities. An **External Advisory Board**, composed of science and technology experts from

academia and industry, will assess the scientific direction and progress of the Center and the Thrusts, and the quality of the scientific program. An **Operational Support** group based in the ORNL Chemical Sciences Division (CSD), reports to the Director. This group supports Procurement, Finance, Environmental, Health, Safety and Quality (ESH&Q), Education and Outreach, Human Resources, and Technology Transfer.

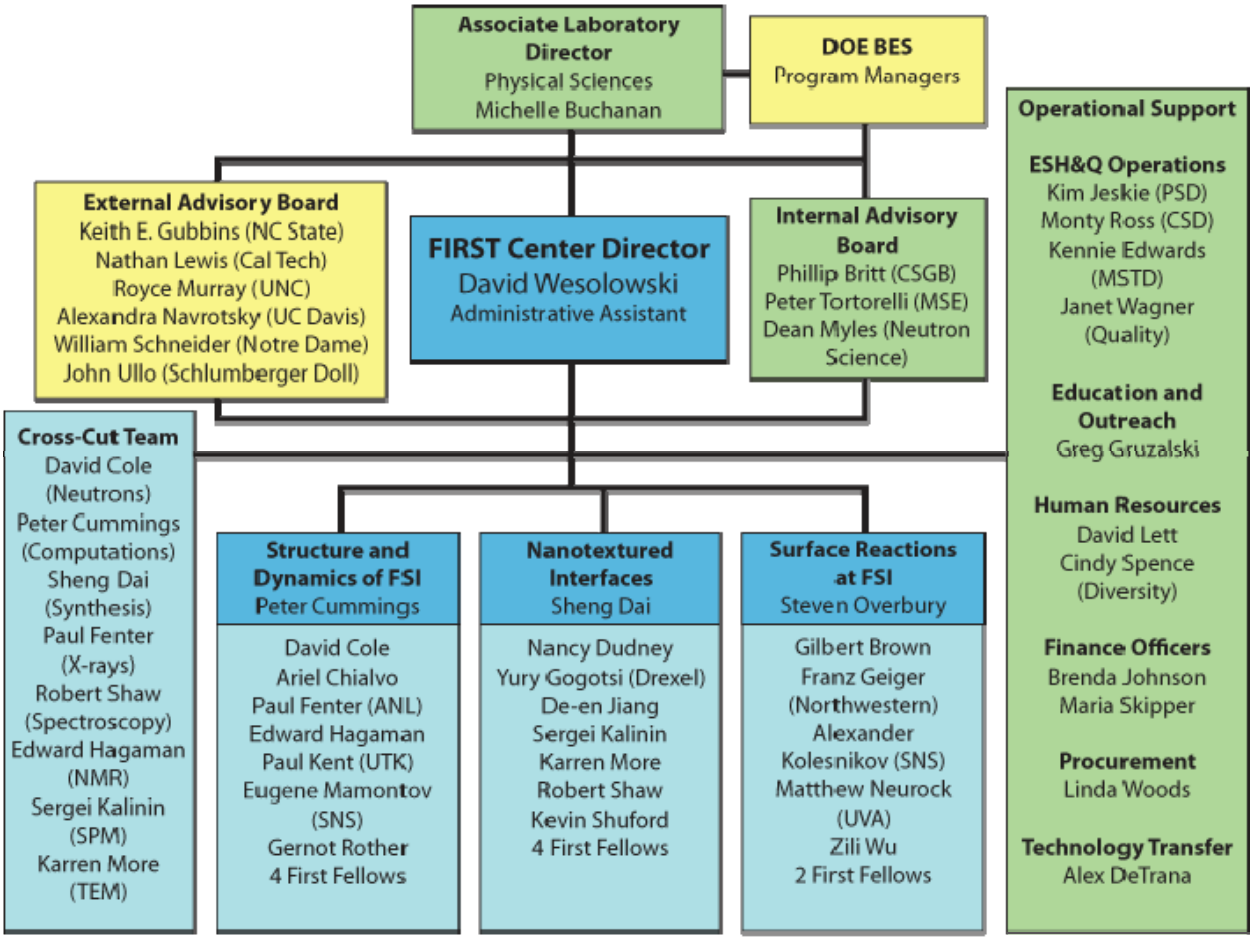

Figure I.3. FIRST Center management structure and primary assignments of researchers and support personnel. (FIRST Research Team in blue, Steering Committee in dark blue.)

Operations: Communication is the key to the successful operation of this Center. The SC will meet at least twice a month to discuss the overall project progress, direction, budgets, operations, and staff and ensure integration among the themes. The ALD and the IAB will be included in one of these meetings. Thrust Leaders will meet with their team weekly to discuss research progress (including student mentoring) and operational issues. External team members will participate via conference call. The entire Center will meet twice a year to discuss progress and cross-cutting themes. Once a year, the SC, IAB, and EAB will meet to review scientific direction, progress and quality of the Center in conjunction with a 2-day, all-hands workshop. At any point in the review process (i.e., the weekly, monthly, or yearly meetings), staff and resources may be reassigned to another task, a task may be eliminated, or a new task may be

created, with the approval of the Director (in consultation with the IAB and ALD), to ensure cutting edge research is maintained with the highest impact.

Scientific Leaders, Qualifications, and Availability: We have assembled a uniquely-qualified team of internationally-recognized experts in order to achieve the ambitious goals of the FIRST Center. Many research team members will participate in thrust areas other than their primary assignments**.** The Director and all Thrust Leaders have significant experience in managing large projects, budgets, and personnel. As staff redirect their efforts to focus on the Center, new staff and postdoctoral researchers will be hired to expand our expertise.

David J. Wesolowski (PI), Distinguished R&D staff in ORNL's CSD, will serve as Director of the FIRST Center, devoting at least 60% of his time to this effort. He is an internationally-recognized expert in interfacial chemistry, fluid speciation, thermodynamics, and heterogeneous reactions. As Lead PI of a large BES Chemical Sciences, Geosciences, and Biosciences (CSGB) project, he has demonstrated his ability to effectively manage a diverse group of scientists from five institutions applying a wide array of advanced experimental, chemical imaging and computational approaches in the investigation of metal oxide-aqueous electrolyte interactions. Wesolowski will reduce his effort in another BES CSGB project to focus on the FIRST Center.

Peter T. Cummings (Co-PI), the John R. Hall Professor of Chemical Engineering at Vanderbilt University, will devote 25% of his time to leading Thrust 1 and coordinating the cross-cut efforts in computational modeling. He is an international expert in molecular modeling of fluids and fluid/solid interactions, and has a joint appointment as Principal Scientist of ORNL's Center for Nanophase Material Science (CNMS, 45%). He currently spends two days/week at ORNL. He will reduce his University teaching duties to focus on this project.

Sheng Dai (Co-PI), Senior R&D staff, will devote 45% of his time to leading Thrust 2 and directing cross-cutting efforts in materials synthesis. He is the Nanomaterials Chemistry Group Leader in the CSD, and Lead-PI on a BES CSGB separations project. He is an expert in synthesis of novel nanoporous materials and ionic liquids. Dai will reduce his efforts on his existing BES projects to focus on the FIRST Center.

Steven H. Overbury (Co-PI), Senior R&D Staff, is the Leader of Thrust 3 and he will devote 45% of his time to the Center. He is the Surface Chemistry and Catalysis Group Leader in the CSD, and Lead-PI on a BES CSGB nanocatalysis project. He has extensive experience in heterogenous catalysis and characterization of surface species. He will reduce his efforts on his current BES project to focus on the FIRST Center.

Cross-Cut Team. The members of the **CCT**, show in **Fig. I.3**, are recognized experts in their particular fields and are matrixed to specific Thrusts. They will be responsible for integrating common experimental and computational techniques across all Thrusts and for developing new techniques to solve complex problems in interfacial science.

External Partners. External experts have been added to complement and enhance our scientific team. **Paul A. Fenter**, the Interfacial Processes Group Leader in ANL's Environmental Research Division, is internationally recognized for promoting the application of synchrotron X-ray scattering approaches in solving complex environmental problems. **Franz Geiger**, the Dow Chemical Co. Professor of Chemistry at Northwestern University, is an expert in non-linear optical spectroscopic studies of interfacial phenomena. **Matthew Neurock**, Joint Professor of Chemistry and Chemical Engineering at the University of Virginia, is an expert in modeling the atomic/molecular phenomena that govern catalytic reactions. **Yury Gogotsi**, Trustee Chair Professor of Materials Science and Engineering, and Director of the Nanotechnology Institute at

Drexel University, is an expert in the development of carbide-derived nanotextured carbons for supercapacitors, gas storage and other applications.

Education and Outreach Coordinator. The operational manager will be **Greg Gruzalski,** coordinating the student and postdoctoral programs and managing the website. He will work with the Steering Committee to develop programs to inspire and train the next generation of scientists with interdisciplinary skills needed to meet the energy challenges of the future.

Commitments from ORNL:

- **Laboratory Director's R&D (LDRD) Program:** Over $8M/year has been invested over the past 4 years on new concepts for Advanced Materials and Interfacial Processes for Energy Conversion. An additional $1.3M was invested in FY08 on research directed toward materials behavior underlying electrochemical performance of advanced batteries. An additional $850K will be invested in FY09 for development of unique capabilities, including high temperature/pressure neutron and X-ray scattering and interfacial chemical probes.
- **Weinberg Fellowship:** A new Fellowship Program named after former ORNL Director Alvin Weinberg has been created to attract outstanding early career scientists with an interest in energy and energy-related research to ORNL, with conversion to staff an option.
- **Laboratory Space:** The FIRST Center will be primarily located in the new $95M Chemical and Materials Sciences building upon completion, and in existing CSD space in the interim.
- **Operational Support:** CSD will provide operational support, including finance, ESH&Q, procurement, human resources, administrative and secretarial support to the Center at no cost.
- **New Staff:** The transition of outstanding FIRST Fellows (see below) and Weinberg Fellows to ORNL staff will be aided with partial support from LDRD funds. These funds would enable pursuit of research on novel concepts not funded by the Center.

Commitments from the State of Tennessee and the University of Tennessee (UT)

- **UT-ORNL Governor's Chair.** Support provided for up to three highly accomplished researchers (Governor's Chair) who will have joint appointments as tenured Professors at UT and Distinguished Research Staff at ORNL. These researchers and their students will conduct research aligned with one or more of the scientific thrusts in the FIRST Center
- **Joint Institute for Neutron Sciences (JINS).** (letter from Egami, **Appendix 9**) Use of the $8.4M JINS facility to serve as an intellectual nexus (with video teleconferencing capabilities) for the integration of neutron sciences into the proposed Center.

Educational Outreach: Our educational outreach activities will focus on training the next generation of scientists (undergraduate, graduate, and postdoctoral associates), in interdependent science, where scientists at the forefront of several disciplines converge to create science that is greater than the sum of the parts, with particular emphasis on inclusion of underrepresented minorities. Since ORNL houses several major national user facilities in neutron science, nanoscience, high performance computing, genomics, and materials science, it is a well established hub of strong educational programs in which many universities and other educational organizations participate. ORNL has had a 60 year relationship with Oak Ridge Associated Universities (ORAU) to advance science training and research programs by providing educational and outreach opportunities for students and teachers at all levels. In 2007, over 230 students participated in internships at ORNL. The FIRST Center, which is composed of a

diverse mix of senior and junior scientists, will work closely with ORAU to recruit outstanding researchers through their research program.

The Center will: (a) provide support to 4 undergraduate students, and 10 postdoctoral research associates per year, all of whom will spend all or part of their time in residence at the Center; (b) strive to ensure diversity in the work force and focus recruiting on underrepresented groups, including women and minorities, utilizing colleges and universities with which ORNL has established productive relationships, such as Tennessee State University, Spelman College, Morehouse College, Fisk University, North Carolina A&T University, Knoxville College, Meharry Medical College, and Jackson State University; (c) establish the FIRST Center Lecture Series and provide funds for international experts from industry, academia and national laboratories to deliver lectures and consult with the research team; and (d) provide travel funds for FIRST team members to visit other institutions and gain critically needed expertise and/or conduct experimental studies at major user facilities.

Promotion of Energy Science and Technology: The primary product of the FIRST Center will be journal and book publications in the peer-reviewed scientific literature and presentations at national and international conferences. The SC and the EOC will also formulate strategies for hosting hands-on workshops at the Center and targeting key conferences for symposia organized and heavily-attended by Team members. We will develop a series of lectures suitable for Departmental seminars and work with our academic partners to develop lecture notes and audiovisual materials for incorporation into undergraduate and graduate courses in chemistry, physics and other relevant fields, focused on interfacial science and energy-related basic research and development. ORNL staff will be encouraged to act as visiting lecturers at our partner institutions and other academic settings. We will also work with ORAU to develop summer projects suitable for high school science teachers, undergraduates, and graduate students. We will establish a publically-accessible website that will contain information about the Center activities, staff, publications, and information related to national energy technology needs.

Relationship of the Proposed Research to Existing and Planned Research Programs at ORNL: ORNL has a large BES CSGB and Materials Sciences and Engineering (MSE) Program that addresses fundamental questions in catalysis, separations and analysis, geosciences, computational chemistry, X-ray and neutron scattering, electron microscopy, condensed matter and alloy physics and material chemistry and synthesis. Currently, there are 13 projects (FWPs) in the CSGB portfolio that cluster around the central theme of molecular transformations and characterization of interfaces. There are 18 FWPs in the MSE portfolio and many projects focus on materials synthesis and nanoscale characterization. These and ORNL's LDRD program provide a large base of technical expertise from which the Center can draw upon.

Environmental, Health and Safety Practices and Oversight: Most of the Center research will be conducted at ORNL under the Integrated Safety Management System. A Research Safety Summary (RSS) will be prepared and approved by the Director and line management for this program that incorporates the scope of the work, the associated environmental, safety and health hazards, and the appropriate hazard controls. No work at ORNL will be preformed outside the scope of the RSS, which will be reviewed and updated annually and whenever a new activity is introduced. All work will be performed in accordance with environmental regulations. A similar ESH program exists at ANL. All of our university partners (UVa, UNC, Drexel, Vanderbilt, Northwestern, UT) have Environmental Health and Safety Offices, and policies and procedures that ensure compliance with local, state, and federal regulations and ensure the health and safety of faculty and students.