ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Laboratory Directed Research and Development Program FY 1998

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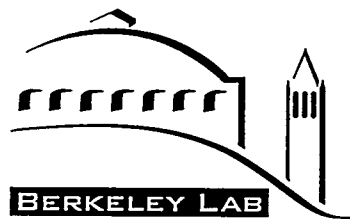
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Report on
Ernest Orlando Lawrence
Berkeley National Laboratory

Laboratory Directed Research and Development Program

FY 1998

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Introduction

The *Ernest Orlando Lawrence Berkeley National Laboratory (LBNL or Berkeley Lab) Laboratory Directed Research and Development Program* FY 1998 report is compiled from annual reports submitted by principal investigators following the close of the fiscal year. This report describes the supported projects and summarizes their accomplishments. It constitutes a part of the Laboratory Directed Research and Development (LDRD) program planning and documentation process that includes an annual planning cycle, projection selection, implementation, and review.

The LBNL LDRD program is a critical tool for directing the Laboratory's forefront scientific research capabilities toward vital, excellent, and emerging scientific challenges. The program provides the resources for LBNL scientists to make rapid and significant contributions to critical national science and technology problems. The LDRD program also advances LBNL's core competencies, foundations, and scientific capability, and permits exploration of exciting new opportunities. All projects are work in forefront areas of science and technology. Areas eligible for support include the following:

- Advanced study of hypotheses, concepts, or innovative approaches to scientific or technical problems;

- Experiments and analyses directed toward "proof of principle" or early determination of the utility of new scientific ideas, technical concepts, or devices; and

- Conception and preliminary technical analyses of experimental facilities or devices.

The LDRD program supports LBNL's mission in many ways. First, because LDRD funds can be allocated within a relatively short time frame, LBNL researchers can support the mission of the Department of Energy (DOE) and serve the needs of the nation by quickly responding to forefront scientific problems. Second, LDRD enables LBNL to attract and retain highly qualified scientists and supports their efforts to carry out world-leading research. In addition, the LDRD program also supports new projects that involve graduate students and postdoctoral fellows, thus contributing to the education mission of LBNL.

LBNL has a formal process for allocating funds for the LDRD program. The process relies on individual scientific investigators and the scientific leadership of LBNL to identify opportunities that will contribute to scientific and institutional goals. The process is also designed to maintain compliance with DOE Orders, in particular DOE Order 413.2 dated March 5, 1997. From year to year, the distribution of funds among the scientific program areas changes. This flexibility optimizes LBNL's ability to respond to opportunities.

LBNL LDRD policy and program decisions are the responsibility of the Laboratory Director. The Director has assigned general programmatic oversight responsibility to the Deputy Director for Research. Administration and reporting on the LDRD program is supported by the Directorate's Office for Planning and Communications. LDRD accounting procedures and financial management are consistent with the Laboratory's accounting principles and stipulations under the contract between the University of California and the Department of Energy, with accounting maintained through the Laboratory's Chief Financial Officer.

In FY98, LBNL was authorized by DOE to establish a funding ceiling for the LDRD program based on 3.5% of LBNL's FY98 operating and capital equipment budgets. This funding level was provided to develop new scientific ideas and opportunities and allow the LBNL Director an opportunity to initiate new directions. Budget constraints limited available resources, however, so only $9.8 M was expended for operating and $0.5 M for capital equipment.

In FY98, scientists submitted 162 proposals, requesting over $25 M in operating funding. Eighty-three projects were funded, with awards ranging from $17 K to $392 K. These projects are listed in the Table of Contents.

Accelerator and Fusion Research Division

Physics and Technology Foundations of a 100-TeV Proton Collider

Principal Investigators: William Barletta, Swapan Chattopadhyay, and Ronald Scanlan

Project No.: 98031

Project Description

Proton synchrotrons based on presently available technology should be able to provide beams in excess of 100 TeV. Proton synchrotrons of even higher energy are possible without undue sacrifice of collider luminosity or unrealistic extrapolation of present technology. The high-energy physics community in the United States appears to be ready to resume consideration of such large colliders in the form of a nationally coordinated research and development program. LBNL is in an excellent position to be the leader of the high-field-magnet aspect of this coordinated effort. This project will involve technical studies aimed at defining the specifications for such synchrotrons.

We will develop the technical parameters needed to establish the practicality of a proton collider at energies much higher than the large hadron collider, now under construction at the European Organization for Nuclear Research (CERN). Because the most cost-critical technical subsystem of such a collider comprises the superconducting dipole magnets, our study will focus on those to a large extent. We will also develop the system framework for studying machine characteristics and set forth the initial physics constraints in the critical areas of beam control and beam dynamics.

Accomplishments

During the past year, we have proceeded on three general fronts:

- The analysis of competing concepts for realizing proton-proton collisions at ≥100 TeV center of mass energy at high luminosity.

- The development of new approaches to reduce the cost of proton supercolliders.

- The specification of critical technology to be developed.

In analyzing the first area, we have extended a spreadsheet-based collider system code to incorporate a detailed model of magnet costs, based on the recent experience at Brookhaven with the fabrication of superconducting dipoles for the Relativistic Heavy Ion Collider (RHIC) project. To allow us to analyze competing approaches using ductile superconductors, we have combined this model with a model of linear costs in the collider. This model is limited in applicability to magnets with ductile materials wound in a cosine coil configuration. To apply the model to use of brittle superconductors in a racetrack coil configuration, we have developed some preliminary notions of how to model such magnets. This model will be developed in parallel with the actual developments of these magnets.

In developing approaches to reducing costs, we have extended the design of a high-field racetrack operating at ~14T to include small apertures above and below the collider beam apertures. See Figure 1. This four-aperture magnet will allow the acceleration of beams over an energy range of more than two orders of magnitude (as compared with the usual factor of ten to twenty). The four-aperture design will eliminate the need for a separate high-energy booster from the injector chain.

All concepts for a future hadron collider appear to require the development of new brittle superconductors, including Nb_3Sn, Nb_3Al, and high-temperature superconductors. Along with collaborators at Fermilab, the University of Wisconsin at Madison, and Texas A&M University, we have produced a detailed program plan and set of specifications to engage industrial superconductor manufacturers in developing scalable, affordable processes to support the program to develop magnets with dipole fields in excess of 10T. We have determined that the present best conductor has a Jc of about $2000 A/mm^2$ at 12T and 4.2 K. Our research and development efforts must next focus on improving the intrinsic
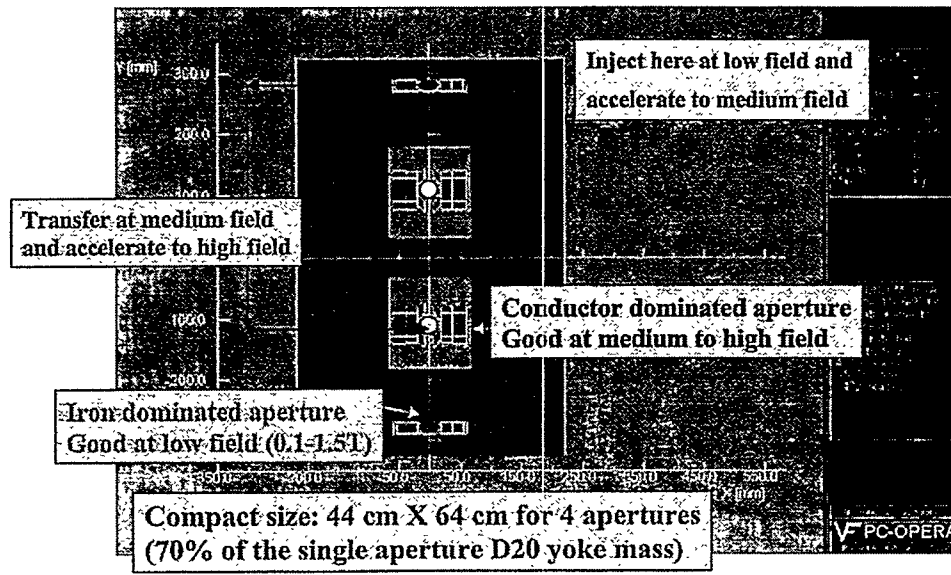
Figure 1. Common coil design magnet system. Return turns of the auxiliary coils (away from the corner) make two low field apertures.

material and wire properties and on small-scale manufacturing, with the goal of coming as close to $3000A/mm^2$ as reasonably possible, while simultaneously improving other parameters such as AC losses and strain resistance. This part of the program may involve some basic work by universities as well as industry and probably will not result in much usable superconducting wire. This proposal was discussed in detail at a recent very large hadron collider collaboration meeting, where our approach was endorsed.

A Combinatorial Approach to Elucidating Melt Texturing of Ag-Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

Principal Investigators: Daniel Dietderich, Xiao-Dong Xiang, Nina Heinig, and Jing Song Wang

Project No.: 98001

Project Description

The goal of this project has been to grow and characterize thick polycrystalline films with stoichiometries around Bi$_2$Sr$_2$CaCu$_2$O$_x$ and, after melt-texturing, to gain a better understanding of the relationship between stoichiometry, heat-treatment, and critical current density. These issues are of continuing interest in developing high-temperature superconducting material suitable for high-field, high-current-carrying applications. This report outlines our accomplishments in this project.

Accomplishments

A number of thick (600 nm) near stoichiometric Bi$_2$Sr$_2$CaCu$_2$O$_x$ films on unheated MgO substrates were grown by pulsed laser ablation (PLD). Immediately after deposition, the samples were annealed *ex situ* for one hour at 810° C. This produced rough-surfaced, polycrystalline films. Films with nominal Bi$_2$Sr$_2$CaCu$_2$O$_x$ stoichiometry were grown, as were several films with composition gradients in Bi, Sr, and Ca. These variable composition films were made using moving shutters and two PLD targets, one of composition Bi$_2$Sr$_{2.3}$Ca$_{0.7}$Cu$_2$O$_8$ and the other of composition Bi$_2$SrCa$_2$Cu$_2$O$_8$.

The films were structurally and chemically characterized by x-ray diffraction, SEM, and EDX. X-ray diffraction showed that all these films have a high degree of texture in the c-axis direction and consist mainly of Bi$_2$Sr$_2$CaCu$_2$O$_x$. The presence of Bi$_2$Sr$_2$CaCu$_2$O$_x$ was confirmed by EDX measurements indicating that pre-melt-textured films consist of Bi, Sr, Ca, and Cu in the stoichiometric ratio of 2:2:1:2. Four-point probe-transport measurements on these

as-grown films show no critical current above 4.2 K, presumably because of the poor connectivity between the superconducting grains.

The samples were then coated with 250 nm of silver, and the samples were melt-textured by heat-treating in flowing, dry air. The peak temperature was varied to determine the optimum melt-texturing temperature. Several films with different morphologies, compositions, and superconducting properties were produced, and these results are summarized in Figures 1 and 2.

A maximum melt-texturing temperature of 891° C led to a Sr-rich, very thin, discontinuous film of $Bi_2Sr_2CaCu_2O_x$, where much of the silver either evaporated or formed isolated islands. Reducing the peak temperature to 881° C and shortening the time at temperature produced a thicker, slightly Cu-rich film consisting of large platelets of $Bi_2Sr_2CaCu_2O_x$. In transport measurements, this film was metallic, had a critical temperature ($T_c > 77$ K) and had a critical current of 800 mA at 4.2 K. Lowering the peak temperature further, to 877° C, appeared to reduce the grain size and degree of texture of the $Bi_2Sr_2CaCu_2O_x$, reduced T_c to 70 K, and resulted in a rather low critical current at 4.2 K of 10 mA. A further reduction in the peak melt-texturing temperature to 875° C gave results much like those at 877° C.

This preliminary work demonstrates the viability of the thin-film approach to correlating composition and superconducting properties in the $Bi_2Sr_2CaCu_2O_x$ material.
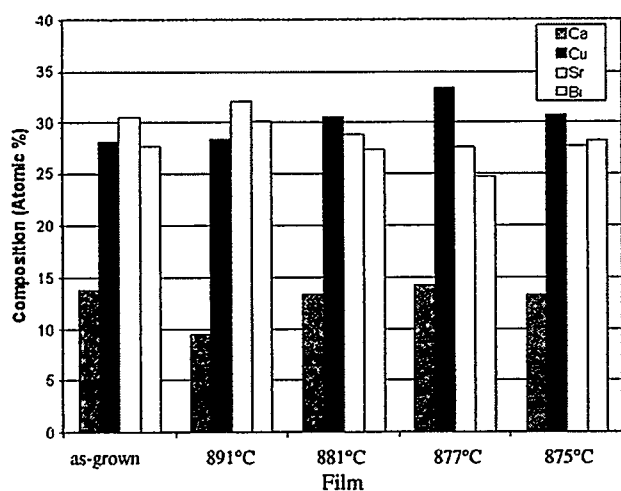
Figure 1. Relative composition of $Bi_2Sr_2CaCu_2O_x$ films melt-textured at various temperatures. Composition is determined by EDX.
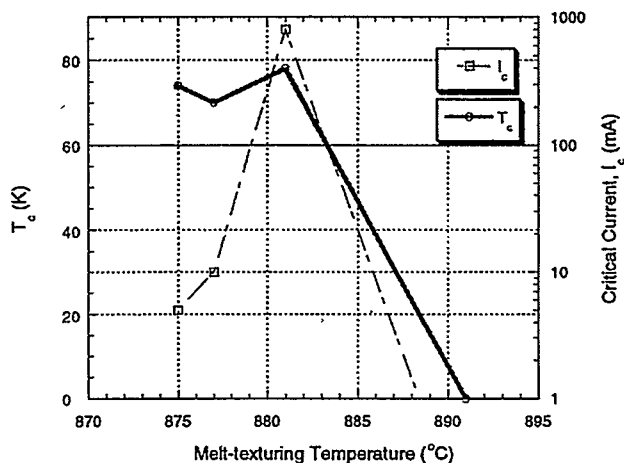
Figure 2. Superconducting critical temperature, T_c, and critical current, I_c, as a function of peak melt-texturing temperature. T_c and I_c are determined by dc transport.

Advanced Induction Accelerators

Principal Investigators: David Anderson, Ka-Ngo Leung, Ramesh Gupta, Edward Lee, and Louis Reginato

Project No.: 98002

Project Description

Induction accelerators, in principle, offer an attractive, elegantly simple solution for many applications. However, the technology of this approach is not well enough developed to compete with the more mature radio frequency (rf) acceleration methods. R&D is needed in pulsers, beam transport systems, and ion sources. For pulsers, we have worked with manufacturers to combine the unparalleled power-handling capability of the silicon-contained rectifier (SCR) with the energy delivery (di/dt) that we need, using magnetic pulse compression. In the area of beam transport, we used a high-T_c superconductor for the first time to build a quadrupole. In our ion source R&D, we used combined electrostatic and magnetic confinement to achieve a high duty factor with a fast rise time.

Pulsers

For two-beam-accelerator (TBA) and heavy-ion fusion, we have used thyratrons almost exclusively for the switches. The heavy-ion fusion program is

working with two manufacturers, English Electric Valve and Triton, to determine whether they can reduce the cost and improve the performance for fusion applications. In many other applications, however, a high pulse-repetition rate and long life are very important. For sheer power-handling capability, high repetition rate, and life expectancy, an SCR is unparalleled. Unfortunately, the SCR cannot now deliver energy (di/dt) at sufficiently high rates. For short pulse requirements, the rate of energy delivery must be increased by factors of 10 to 50. Good progress has been made in the last decade, but more is needed. The application of nonlinear magnetic pulse compression may enable the fastest SCRs to be used. This project carried out a development program, in conjunction with the manufacturers, to determine whether SCRs and magnetic pulse compression will provide a good solution to the switching problem.

Beam Transport Systems

Induction accelerators have usually used dc normal-conducting solenoids for beam transport. For heavy ion fusion, we have used electrostatic quadrupoles and had planned to use pulsed normal quadrupoles for our next experiments; but in the long term, induction accelerators would benefit from superconducting transport systems. However, the design of a cryogenic and support system for superconducting magnets with the warm bores required for this application (in contrast to the cold bores of high-energy physics accelerators) is a major challenge and cost issue. The new high-T_c superconductors would be a natural choice for solving this problem.

Ion Sources

In this area, we continue to develop a high-duty-factor gas ion source that is capable of producing fast-rising beam pulses for induction linac applications. Ion beam pulses that have a fast rise time ($\leq\mu s$) will minimize the volt-seconds needed from the induction cores and pulsers, thus making them cheaper and easier to design. The beam pulse length should be on the order of tens of microseconds.

At present, fast rise time is obtained by controlling the high-voltage pulses applied to the extraction gas immediately outside the source aperture. This method works well for producing electron beams or heavy ion beams (e.g., Cs^+ and K^+). Both types of beams use surface-conversion-type sources. However,

to produce beams of interesting ions, including protons or high-charge-state ions, a gas ion source is more appropriate. Unfortunately, the conventional gas ion source has a slow rise time, limited by the plasma formation time. Shortening the rise time by controlling the extraction gap voltage (and having the plasma turned on ahead of time) is not always successful, because the plasma prefills the extraction gap and may cause premature gas sparkdown. Our new approach will keep both the plasma and the extraction voltage running in steady state but control the plasma flow (into the extraction gap) by a combination of magnetic and electric confinement.

Accomplishments

Pulsers

Advanced components for the critical functions of energy switching and storage were evaluated. The cost for the thyratron devices suggested by the two companies differs by a factor of two. Otherwise, these devices are very similar in voltage, di/dt, and lifetime, and both consist of three gaps with a ceramic envelope.

Solid-state switching offers potentially unlimited life. However, the additional cost of going to higher di/dt, the voltage needs, and the optimization requirements for the manufacturing process require further study before these thyratron devices can be considered for inclusion in a full-scale linac. In addition, capacitors for energy storage exist today for the short pulses. Optimization in manufacturing processes or adaptation of power factor capacitors should reduce the cost to less than $1.00 per joule. Finally, the cost per joule for switching the stored energy appears to be between $3.00 and $6.00. This estimate is based on diligent studies, and no great advances are expected in the future.

Beam Transport Studies

A high-T_c quadrupole magnet concept was developed for beam transport. We built a five-turn coil using a prereacted tape (BSCCO-2223) purchased previously from American Superconductor Corporation. (The tape measured 2.7 mm wide and 0.2 mm thick.) The coil had a circular (solenoid) geometry with a minimum bend radius of 40 mm. The insulation was fed from a smaller reel, and the HTS tape from a larger one. A small amount of winding tension was applied through the insulator. We also performed a series of other experiments with a small, straight section of this tape. In addition, we examined the

effects of varying the bend radius. In all cases, the samples were tested at liquid-nitrogen temperature for faster turnaround.

The tape in this coil was observed to have a J_e of 76 A/mm^2 (not including the reduction due to the insulation we added). This is almost the same value we expected to find in a tape having no degradation. On the basis of this value, we would expect to achieve a J_e of ~ 200 A/mm^2 at 4° K using known extrapolation and assuming no degradation. The tapes available today are about two times better than the tape we used in our experiments; thus, the overall current density (including insulation) used in our model calculations was more optimistic by about a factor of three than if based on tapes now available.

The proposed design based on HTS appears to be promising. Given the rapid rate of progress in this field, an overall current density of 500 A/mm^2 at 20 K seems to be a reasonable assumption for a future magnet system.

Ion Sources

The source used in the measurements was a standard 10-cm multicusp source with rf discharge. Preliminary results demonstrated current densities of more than 400 mA/cm^2 at rf-power levels of 20 kW using neon discharge. With heavier elements such as Ar, Kr, and Ne, current densities of 200–300 mA/cm^2 were reached at the same extraction voltage of 20 kV.

The beam emittance was measured by means of a pepper-pot device. This consists of a tantalum plate in which four rows of very small apertures (0.2-mm diameter) were drilled in a certain pattern. A film was positioned at a distance of 50 mm from the entrance plate to be exposed by the beamlets. From the exposed pattern, the beam emittance can be determined. Preliminary results from a cw argon beam show that the normalized emittance is on the order of 0.03 mm mrad.

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Laser-Driven Acceleration of Particles

Principal Investigators: Wim Leemans, Jonathan Wurtele, and Swapan Chattopadhyay

Project No.: 97002

Project Description

This project is an experimental and computational study of a particle accelerator based on ultra-high-gradient (tens of GeV/m), laser-driven acceleration over long distances (1–10 cm) in plasmas. Experimental techniques are being developed to (1) channel ultra-high-intensity laser pulses in centimeters-long, laser-produced plasmas; (2) excite, probe, and control longitudinal wakes with multi-GeV accelerating gradients in these plasma channels; and (3) inject femtosecond-long electron bunches into the channel. For fast and accurate modeling of the experiments, numerical tools and computational codes are being developed and integrated with the experimental program. This work may lead to future compact accelerators using plasma or other advanced accelerator concepts.

Accomplishments

Experiments

During FY98, a terawatt laser system based on chirped-pulse amplification has been completed in the Laser Optics Accelerator Systems Integrated Studies (l'OASIS) lab at the LBNL Center for Beam Physics. The present system produces a short pulse (<75 fs) with a peak power of up to 1.5 TW, a center wavelength around 0.8 μm, and a 100–250 ps long pulse containing up to 300–400 mJ at 0.8 μm. This laser system has been used for producing plasma channels as well as guiding high intensity laser pulses.

Laser guiding over distances comparable to the diffraction distance (Rayleigh length) of a focused laser beam is essential for the development of long-scale-length, laser-driven particle accelerators. As part of this project, plasma channels have been developed and used to guide high-intensity pulses. The following milestones have been achieved:

- A new technique for plasma channel creation has been developed: the ignitor–heater scheme.

- Guiding of the highest-intensity (5×10^{17} W/cm^2) laser pulses to-date (in a plasma channel with appropriate transverse plasma density profile and size) has been achieved.

The ignitor-heater scheme makes use of two laser pulses: (1) the ignitor, an ultrashort (<100 fs) laser pulse to preionize the plasma; and (2) the heater pulse, a long (200 ps), energetic (100–300 mJ) pulse to heat the plasma. The heating leads to an exploding plasma fiber channel with a density minimum on-axis. Such a channel has properties of an optical waveguide. The unique features of this ignitor-heater technique are:

- The possibility of creating plasma channels in low-atomic-number gases, such as hydrogen, which is important for guiding highly intense laser pulses.

- A reduction in the required laser-pulse energy by a factor of 2–3 compared to conventional single-pulse channel-formation methods.

- Channel profile control: slab-like and cylindrically symmetric channels have been produced.

To implement the ignitor-heater channel-creation scheme, the two laser pulses were combined in a line-focus by means of cylindrical optics onto a gas jet. See Figure 1. The gas jet was used to avoid ionization-induced refraction in a statically filled experimental chamber.

To evaluate the guiding properties of the channels, we injected high-intensity laser pulses into the plasma channel and imaged them onto a charge-coupled device camera. The laser pulse (injection pulse) was

focused near the entrance of the channel, using an off-axis parabola. The time delay between the ignitor pulse and the injection pulse was fixed to 600 ps. Figure 2 shows images of the injection laser pulse (a) propagating through a vacuum (with the gas jet turned off), (b) after undergoing ionization-induced refraction in the gas jet plume without the presence of the heater pulse (and thus no formation of a channel), and (c) guided by the channel for a gas jet backed with nitrogen at 1000 psi. Vertical lineouts of images of Figure 2 clearly demonstrate the changes induced by the plasma channel on the guided laser pulse. The change in size of ~8 times is consistent with a laser beam of Z_R~0.1 mm propagating a distance of 0.8 mm (the width of the jet), i.e., 8 Rayleigh lengths. Experiments on producing >1 cm gas jets are underway.

Plasma channels were created in an elongated, elliptical shape for the specific ignitor and heater pulse parameters. In turn, the guided beam images (Figure 2) had a similar elongated shape. Through control of the ignitor pulse intensity, we created channels with circular cross sections, possessing guiding properties in the X as well as Y directions.

Theory

During FY97, in collaboration with colleagues from the Naval Research Laboratory, we proposed a novel
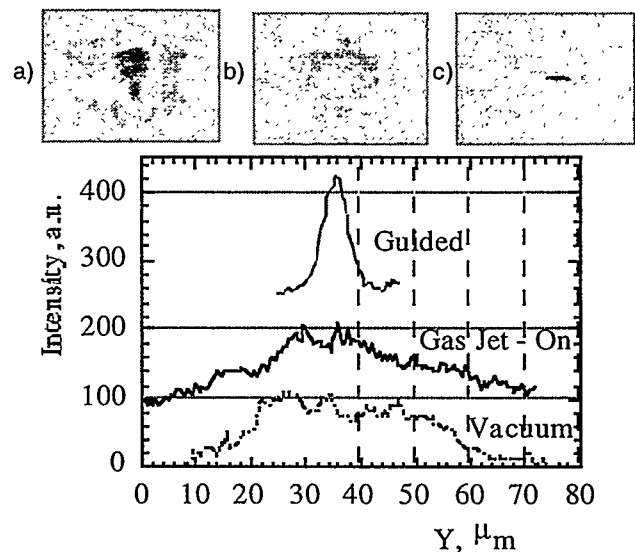
Figure 2. Laser beam images and vertical lineouts pulse a) gas jet turned off, b) gas jet turned on without heater pulse, and c) guided by the channel, for a gas jet backed with nitrogen at 1000 psi.

Figure 1. Experimental setup.

scheme for particle injection into plasma wakes based on a colliding laser pulse scheme.

During FY98, detailed particle-tracking simulations in three dimension have been performed to further evaluate the colliding-laser-pulse scheme. This colliding-pulse scheme, which uses three laser pulses, has the ability to produce femtosecond electron bunches with low fractional energy spreads, using relatively low injection laser pulse intensities compared to the pump laser ($a_{inf}^2 \ll a_{pump}^2 = 1$).

Here

$$a = eA / mc^2 \cong 8.5 \times 10^{-10} \lambda[\mu m] I^{1/2} [W / cm^2]$$

is the normalized vector potential, with I the laser pulse intensity and λ the laser wavelength.

When the injection pulses collide (some distance behind the pump) in the plasma wake of the pump laser, they generate a slow-phase-velocity ponderomotive beat wave. This beat wave can cause electrons, undergoing a plasma oscillation caused by a_0, to acquire a momentum and phase change sufficient for trapping.

To study the detailed properties of the electron bunches, we performed three-dimensional simulations using prescribed fields for the laser beams and plasma wakes. Figure 3(a) shows the fraction of loaded test electrons that become trapped and focused, as well as the bunch duration for trapped electrons versus the beat-wave-amplitude parameter. As an example, for a plasma density of $n_e = 7 \times 10^{17}$ cm^{-3}, the maximum fraction corresponds to a bunch number of $N_b = 0.5 \times 10^7$ electrons. Note, however, that larger numbers of electrons can be trapped by increasing the laser spot size or by increasing the plasma density.

Figure 3(b) shows the asymptotic fractional energy spread $\sigma_\gamma / \langle \gamma \rangle$ and the transverse normalized rms emittance of the electron bunch versus the beat-wave-amplitude parameter. As expected, the rms phase spread (bunch duration) is constant for a highly relativistic bunch, the fractional energy spread is asymptotic for large interaction lengths, and the transverse normalized rms emittance is conserved for large pump laser spot size. In summary, generation of electron bunches with $\tau \approx 3$fs, $\sigma_\gamma / \langle \gamma \rangle \approx 1\%$ and $\varepsilon_\perp \approx 1\pi$ mm-mrad appears possible.

Modeling of laser propagation in plasma channels has resulted in a better understanding of laser coupling efficiency, modal losses and leakage, wake excitation, and group and phase-velocity dispersion.
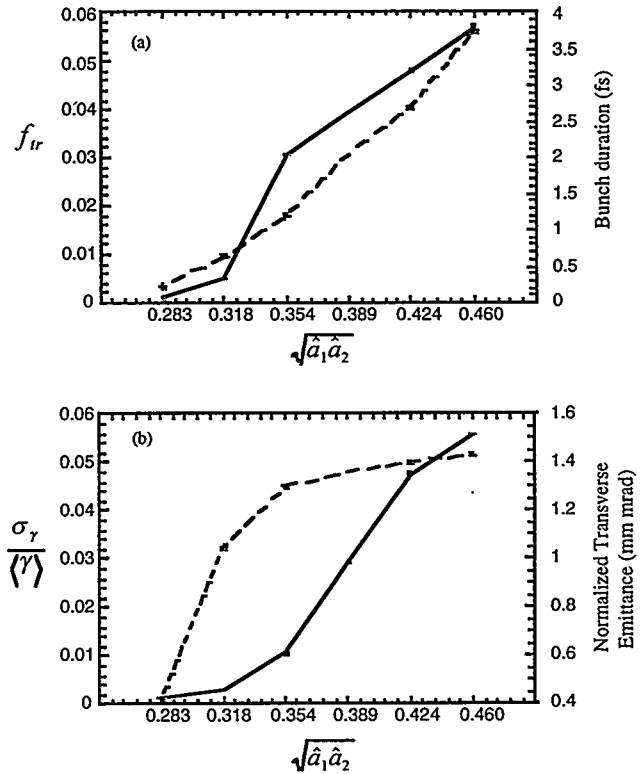
Figure 3(a). The fraction of loaded test electrons that become trapped and focused, and the bunch duration for trapped electrons versus the beat-wave amplitude parameter. (b) Asymptotic fractional energy spread and transverse normalized rms emittance of the electron bunch versus the beat-wave amplitude parameter.

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Interaction-Point Physics and Optimization of Multi-TeV Linear Colliders

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Principal Investigators: Ming Xie, Tomomi Ohgaki, Hitoshi Murayama, James Siegrist, William Barletta, Swapan Chattopadhyay, John Corlett, and Kwang-Je Kim

Project No.: 98003

Project Description

The interaction point (IP) of a linear collider is the point at which intense beams from the accelerator are brought into collision. It is an interface between particle physics and collider technology. The collision processes occurring at the IP will, on the one hand, directly affect the detector environment and the particle physics under study and, on the other hand, put technical constraints on collider design as a whole. As future linear colliders are pushed into higher energy with higher luminosity, collisions of more intense beams are required. As a result, the study of IP physics is becoming more important. One of the most important constraints on the performance of an e^+e^- linear collider is that imposed by the quantum electrodynamics (QED) processes at the IP, in particular beamstrahlung. This is the synchrotron radiation produced by the particles of one beam as they pass through the electric and magnetic fields of another oncoming beam. Because of the extremely high charge density, the fields can be so strong that colliding particles may lose a significant amount of their energy and suffer severe luminosity degradation. The photons generated by beamstrahlung may also turn to copious e^+e^- pairs, or even hadronic jets, causing troublesome background problems. Therefore, to assess the potential of future linear colliders, it is crucial to identify operation regimes and approaches that minimize the impact of these deteriorating effects on collider performance, taking into account other collider constraints and requirements.

To suppress beamstrahlung, the so-called flat-beam approach has been adopted in all current designs for linear colliders at a center-of-mass energy around 0.5 TeV. However, 0.5 TeV energy is only a near-term goal for linear collider development, very much limited by the current technologies. The flat-beam approach will become more difficult technically and less effective at higher energies. The purpose of this project is to carry out an integrated and comprehensive evaluation of an innovative IP scheme known as quantum suppression of beamstrahlung (QSB) for higher-energy linear colliders. Unlike all other approaches, QSB is effective only when the beam field is sufficiently strong. In this regard, it is compatible with the ever-increasing beam density required of a linear collider at higher energies. We propose not only to treat the subject from the point of view of beam physics, but also to analyze its consequences in terms of detector backgrounds and learn what the implications are for the particle physics to be studied. Another component of this project is to investigate the accelerator physics and the technology issues related to linear colliders and to identify specific engineering tasks by which LBNL could make significant contributions toward achieving an optimized collider system.

Accomplishments

A complete case study was carried out step by step with Monte-Carlo simulations to evaluate the feasibility of QSB. The study covered a comprehensive range of evaluations, from intense beam-beam interaction to QED background assessment and from hadronic event generation to detector simulation. In carrying out this case study, special attention was given to hadronic processes. Current theory on the hadronic minijet cross section is subject to significant uncertainty at higher energies, where experimental data are not available. To reduce this uncertainty, we surveyed different models for both hard and soft strong photon-photon interactions and proposed a recipe for more realistic upper estimates for the cross section. With this recipe, an evaluation of hadronic backgrounds is also given for the Next Linear Collider. In addition, effects of backgrounds on possible cases of particle physics are also considered.

Several potential areas in collider design optimization and engineering have been identified in which LBNL could play a major role in the upcoming international collaboration on linear collider research and development. These areas include damping rings, rf distribution waveguides and mode converters, modulators for dc power, mass production techniques for the net shape production of vacuum-specification copper for accelerating cells, localized and low-duty-cycle electronics and cable plant, and radiation-hardened electronics. In particular, experiments on accelerator physics were performed at the High Energy Accelerator Research Organization of Japan Accelerator Test Facility (KEK ATF) damping ring by an LBNL physicist in collaboration with the Stanford Linear Accelerator team to study several issues for the Next Linear Collider, including damping ring physics, detectors and monitors, and beam diagnostics.

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T. Ohgaki, "Study of Hadronic Backgrounds in Future Linear Colliders," Talk presented at Workshop on Physics and Detectors for Future e^+e^- Linear Colliders (September 26–29, 1998).

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Advanced Light Source Division

Ultrafast X-Ray Spectroscopy Via Optical Gating

Principal Investigators: Thornton Glover, Philip Heimann, Howard Padmore, Robert Schoenlein, Alexander Zholents, and Max Zolotorev

Project No.: 98032

Project Description

Although synchrotrons have provided a wealth of information about the static properties of materials important to the physical and life sciences, inadequate time resolution has limited their role in the study of material dynamics. The ability to perform x-ray spectroscopy with sufficient time resolution to observe the fast (~100 fs) primary events that drive many interesting chemical reactions and phase-transitions will have an important impact on a number of fields in physics, chemistry, and biology. The goal of our research is to expand capabilities at the Advanced Light Source (ALS) for performing ultrafast x-ray spectroscopy by developing a fast (femtosecond) x-ray detector based on optical gating.

Optical gating will be based on laser-induced modifications of an x-ray photoelectron energy spectrum (XPS). Narrow-band synchrotron light (tuned to a k absorption edge) will be used to produce a narrow photoelectron peak. The XPS will be modified, however, if this x-ray ionization event occurs in the presence of an optical (laser) field. Additional peaks (spaced by the optical photon energy) appear on either side of the primary x-ray peak due to scattering (absorption and emission) of optical photons.

The demonstration of optical gating will proceed in two stages: (1) construction and commissioning of a suitable electron spectrometer and (2) observation of laser-induced modifications to an XPS. The electron spectrometer must be optimized for laser-synchrotron experiments and account for a number of factors, e.g., mismatch between the laser and synchrotron repetition rates (five orders of magnitude), mismatch between laser and x-ray pulse durations (two to three

orders of magnitude), and the requirement of good spatial and temporal overlap of x-ray and laser pulses on the sample. These factors dictate use of a detector with high collection efficiency. Because hemispherical analyzers have relatively poor collection efficiency, we have chosen to construct a detector based on time-of-flight spectroscopy, using a high collection efficiency electron mirror. Given the quasi-DC nature of the ALS, the detector will be pulse-biased and we will make use of the "cam-shaft" mode of ALS operation. Once an appropriate XPS has been recorded, a femtosecond laser pulse will co-propagate along with the x-ray pulse to modify the XPS. The final stage of the project will be to use the detector to observe fast structural changes in a (femtosecond) laser heated semi-conductor.

Accomplishments

Since the beginning of project funding in March 1998, a high collection efficiency electron mirror has been designed and constructed that serves as the basis for the electron spectrometer. To date, the spectrometer has been constructed and is in the process of being commissioned. Additionally, data acquisition hardware has been obtained, and the data acquisition software is in the final stages of development.

High-Efficiency Electron-Spin Detector for Photoemission Experiments at ALS

Principal Investigators: Zahid Hussain and Zhi-xun Shen

Project No.: 98033

Project Description

Over a decade after the discovery of high-T_c superconductors, neither the origin of the superconductivity nor the nature of the peculiar normal state in these materials is satisfactorily understood. The heart of this problem lies in the larger problem of understanding highly correlated

materials, which also includes colossal magneto-resistance materials and half-metallic ferromagnets. Further understanding the nature of these materials depends on improved characterizations of their properties—in particular the discovery of new electronic states of matter.

Studies are currently underway at the Advanced Light Source (ALS) to study highly correlated electronic materials, with emphasis on transition metal oxides (e.g., high-T_c superconductors), alloys, and compounds. The objective of this project is to build a high-efficiency electron-spin detector that will become an integral component of the high-energy-resolution spectrometer (HERS) at ALS Beamline 10. This system is the photoemission end station for the study of highly correlated electronic materials. With this new capability, we should be able to discover the d-wave structure in the superconducting pairing state and the normal-state excitation gap. Such measurements in turn would have a profound impact in the field by suggesting a paradigm for superconductivity different from the Bardeen-Cooper-Schrieffer paradigm of the past four decades.

Accomplishments

The project was funded near the tail end of FY98. During this short period, the project began to build the electron-spin detector. The design of the electron-spin detector has been completed (see Figure 1), and an order has been placed for fabrication of the unit. The spin detector is the so-called "min-Mott" type, but it also incorporates several novel features that

Energy analyzer exit plane
ESA entrance slit
3 mm x 10 mm
Electron beam path
Electron Lens system
Rotary Stage
90° Deflector
Gold foil Scattering target
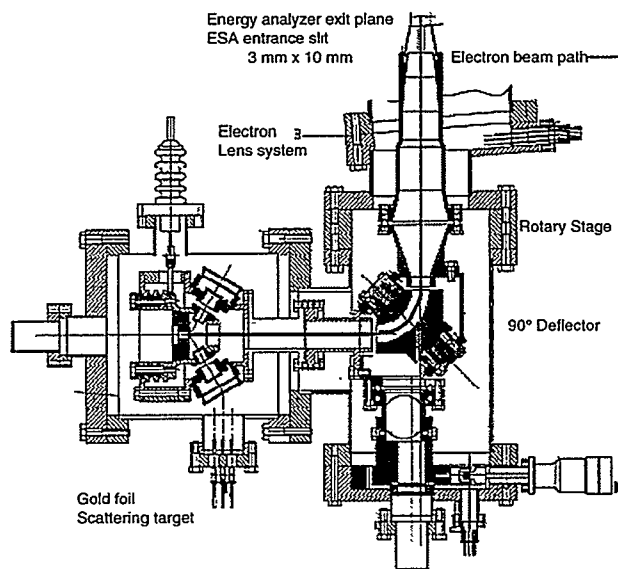
Figure 1. Design for electron-spin detector.

improve the detector efficiency by at least a factor of 30 compared to conventional designs. Its precision lens systems and 90° deflector allow measurement of all three orthogonal components of the electron spin. The spin detector will mount to the exit plane of the high-resolution hemispherical Scienta analyzer and will allow us to measure the spin of the electron with high-energy resolution comparable to kT (about 25 meV at room temperature)—a capability that will make this system state of the art.

A Next-Generation Synchrotron Light Source

Principal Investigators: Alan Jackson and Malcolm Howells

Project No.: 98004

Project Description

The purpose of this project is to develop ideas that will push photon science beyond what existing third-generation light sources are presently achieving. Because ideas based on free-electron-laser (FEL) concepts are being vigorously pursued at other laboratories, we concentrated our efforts directly on lower-emittance beams from rings and/or on beams with much shorter bunch lengths than are available at existing facilities (e.g., ≈ 40 ps FWHM). Rings have an advantage in that source characteristics can be tailored to specific experimental requirements. Our approach included a parallel look at source technology and discussions with the photon user community to identify future needs.

Accomplishments

The main challenges associated with ring-based systems were traced to (1) chromatic correction (sextupole distributions) and dynamic aperture, (2) emittance growth due to intra-beam scattering, and (3) short Touschek lifetime. Issues (2) and (3) are related because they involve different magnitudes of Thomson scattering of electrons within a single bunch. This relationship was investigated in detail, and an enhanced formalism that includes (for the first time) all three dimensions of the beam was developed. This formalism was checked against measurements made at the Advanced Light Source

(ALS). One solution to the short Touschek lifetime is to lengthen the bunch (thereby reducing the bunch density) using a higher harmonic rf cavity. Simulation tools were developed to study the efficacy of this approach. The same tools were later used to specify the requirements for a third-harmonic cavity system for the ALS. This is now a fully funded ALS-Accelerator and Reactor Improvement Modification (ARIM) project. Studies associated with chromatic correction and dynamic aperture had to be abandoned when manpower was redirected to other projects. These still remain issues for ultra-low-emittance beams.

Through informal discussions with the ALS user community and interested parties at LBNL and on the UC Berkeley campus, we discovered a large community interested in x-ray pulses with pulse lengths on the order of 100 fs. This community was significantly larger than those interested in lower-emittance beams, so we began to focus more attention in this direction. We established parameters that would be desirable in a "femtoscience facility":

- Energy range: 1 to > 10 keV
- Flux: 10^9 photons/sec; in a bandwidth ($\Delta\lambda/\lambda$): 10^{-3}
- Pulse width: < 200 fs FWHM
- Acceptable repetition rate: < 100 kHz
- Sample size: $\approx$ 100 μ/side
- Angular subtend: < 1 mrad
- Synchronization: < 100 fs, with respect to a "pump" pulse

Several accelerator-based schemes for producing x-rays with the characteristics described above are now under study. They are at the conceptual design level, with much more work required before their performance can be assessed.

Publications

C.H. Kim, "A Three-Dimensional Touschek Scattering Theory," *Particle Accelerators* (submitted).

A. Jackson, "Report on the Workshop on the Uses and Generation of Femtosecond Radiation," LBNL-42093 (1998).

Development of an Aberration Corrected Photoelectron Microscope for Surface Studies

Principal Investigator: Howard Padmore

Project No.: 97003

Project Description

The goal of this project is to develop an aberration balancing scheme for a full-field photoemission microscope. The first year of the project concentrated on developing a full theoretical model of the aberration corrector and its operation in a 30-KV microscope. The second year has involved the complete design of the aberration corrector's magnetic separator and electron mirror as well as a detailed study of the aberrations of an uncorrected PEEM. Photoemission electron microscopy (PEEM) involves illuminating a field, typically 30 μm in diameter, and imaging the emitted photoelectrons. In conjunction with tunable, high-brightness synchrotron radiation, this imaging method can be combined with spectroscopy by recording images at successively higher photon energies through an absorption-edge region. X-ray absorption spectroscopy gives detailed information about chemical state at the surface and, combined with high-resolution imaging, becomes a powerful tool in investigations of surface chemistry. The limitation of the technique is its restricted spatial resolution, typically 0.1 μm. This limitation is caused by the combination of the chromaticity of the electron microscope lenses with the energy spread of the photoemitted electrons. The aim of this project is to overcome this limitation by aberration balancing.

Accomplishments

Our existing un-aberration corrected PEEM has been completed, and its resolution and imaging characteristics have been thoroughly measured. This characterization has allowed us to determine the extent of the aberrations to be corrected and evolve the best overall strategy. The resolution of this system has been measured at 40 nm with x-rays and is one of the highest resolution systems built to date. The use of a chromatic and spherical aberration corrector will allow a resolution of 1–2 nm to be achieved if

mechanical stability issues can be resolved. This will be a revolution in the application of synchrotron radiation to the study of surfaces. The key component is the separator magnet; detailed design is finished, and we are proceeding to construction with follow-on funding. In collaboration with Arizona State University, IBM (Almaden), and the Synchrotron Radiation Research Center (Taiwan), we are proceeding now with construction of a full-prototype system that should be capable of nm resolution. In parallel, we are applying to NSF for funding of the production microscope and to DOE for the funding of the undulator and beamline source.

Publications

S. Anders, H.A. Padmore, R.M. Duarte, T.R. Renner, T. Stammler, and A. Scholl, "Design and Performance of a New Photoemission Electron Microscope for the Study of Magnetic Materials" (submitted to *J. Appl. Phys.*).

Studies in Beam Dynamics and Operations with Superconducting Magnets at Critical Energy of 12 keV at ALS

Principal Investigators: David Robin and Ronald Scanlan

Project No.: 98034

Project Description

The concept of implementing superconducting magnets to enhance the capabilities of the Advanced Light Source (ALS) has been endorsed by the ALS Science Policy Board, the Workshop on Scientific Directions for the ALS, the ALS Science Advisory Committee, and DOE/Basic Energy Sciences (BES). A significant fraction of the ALS user community is interested in using high-brightness, intermediate-energy x-ray light from such superconducting magnets for applications such as protein crystallography, submicron-spot-size x-ray diffraction of heterogeneous materials, and submicron-spot-size

x-ray absorption on environmental and earth-sciences samples.

It appears likely that a magnet can be built with a sufficiently robust operating margin. The purpose of this project is to study the beam dynamics and operation through building and testing a proof-of-principle model, including tests of the cooling system and current leads. Also, accelerator-physics simulations are being performed to study the impact of superconducting on machine performance (dynamic aperture).

Accomplishments

A conceptual design of the cryosystem has been made. Two of the key features of the system are the cryocoolers and the leads. We have chosen a Gifford McMahon (Sumitomo 1.5-W) cryocooler without a Joule Thomson (J.T.) circuit. This cooler is regarded as much more reliable than cryocoolers with J.T. circuits and is commonly used in magnetic resonance imaging (MRI) machines. In addition, we have chosen high-temperature superconducting (HTS) leads. HTS leads exhibit very low heat leak compared to normal conducting leads, a feature essential for operation.

Currently, LBNL (in conjunction with Wang MRI) is performing experiments to test the proposed cryo-cooler/HTS lead combination. A Sumitomo 1.5 W cryocooler and HTS leads have been purchased, and a cryostat is being built. This experiment will test system reliability, heat leaks, and thermal characteristics, as well as train operators in cryocooler operation. Results should be obtained in early 1999.

During 1998, we have done considerable work to study the impact of the magnets on beam dynamics. Of particular concern are the magnets perturbing the ring's natural 12-fold symmetry and impacting the stability of the particle motion. (Having three superconductor magnets reduces the symmetry of the ring from 12 to 3.) One of the methods used to visualize the impact of symmetry breaking is Frequency Map Analysis. Figure 1 shows tunescans with 0, 4, 3, 2, and 1 superconducting magnets in the lattice. The results of the tunescans and other tracking studies indicate that three magnets cause increased resonance excitation and chaotic motion when the ring symmetry is broken. We still might find working conditions where no significant effect on the ring performance (injection and lifetime) occurs.

No Superconducting Magnets

4 Superconducting Magnets

3 Superconducting Magnets

2 Superconducting Magnets

1 Superconducting Magnet
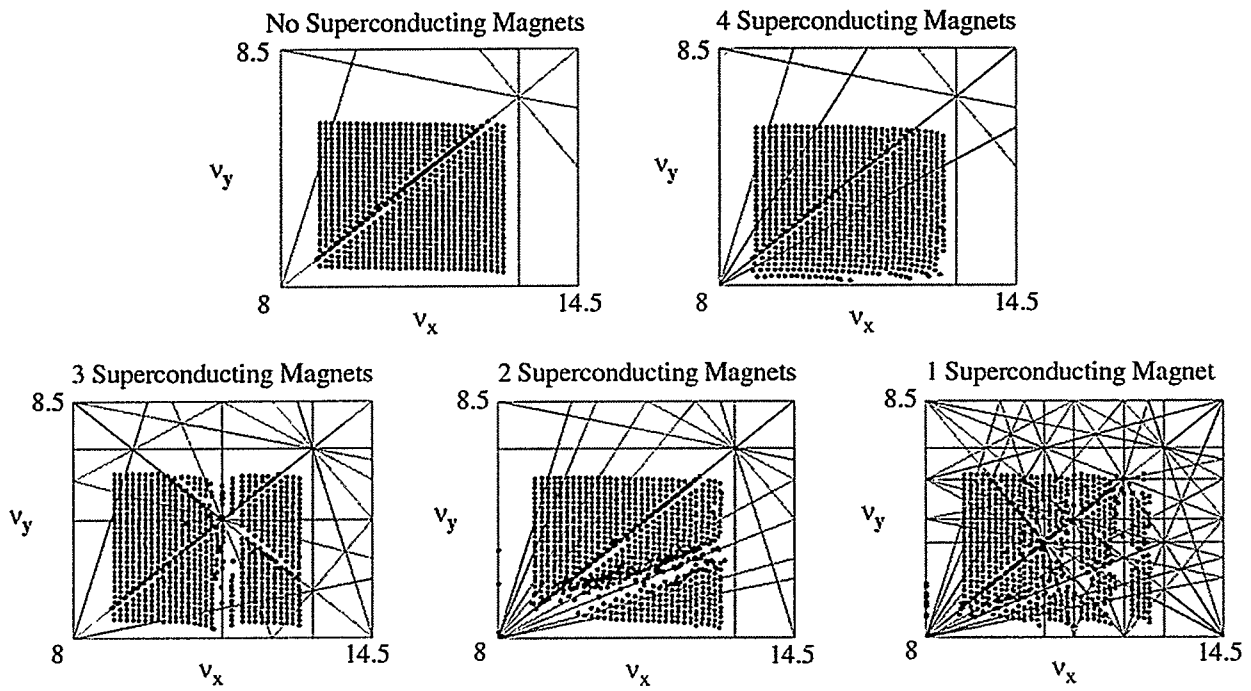
Figure 1. Horizontal and vertical tunescans versus different numbers of magnets. Missing and nonuniformly place points indicate chaotic zones.

Chemical Sciences Division

Network Silicates with Porphyrin Backbones: Novel Solids and Catalysts

Principal Investigator: John Arnold

Project No.: 96003

Project Description

The ability of chemists to control chemical and physical properties on the molecular scale has been the major driving force in synthetic chemistry over the last hundred years. It is only quite recently, however, that attention has focused on more complex supramolecular systems, where small molecules are used as templates for the synthesis of complex two- and three-dimensional framework structures. We intend to lead this research into a new area of study by fabricating robust arrays incorporating porphyrin backbones, held together by strong siloxane linkages built using sol-gel chemistry. If this approach is successful, it will lead to a new class of materials, engineered by molecular chemistry to control structural relationships and pore sizes.

In concert with building new supramolecular compounds, this chemistry will be applied to the preparation of new heterogeneous porphyrin-based catalysts for alkane oxidation and olefin epoxidation.

Over the years, numerous models have been prepared in an attempt to mimic enzyme active sites such as those in cytochrome P-450. To prevent degradation of the catalytically active site, nature uses protein sheaths to control the local environment. We propose to exert similar control by building frameworks using the chemistry described in this report. Because these systems are based on molecular chemistry, they combine the attractive features of both homogeneous catalysts (primarily "tunability" and control of the catalyst center) with those of solid-phase heterogeneous catalysts such as aluminosilicates. This synergism between homogeneous and heterogeneous catalysis may result in the development of a new range of highly selective, environmentally benign catalysts.

In addition to the catalytic potential of these compounds, we envisage a number of other interesting applications, including potential uses as sensors, large-pore molecular sieves, and magnetic and conducting solids.

Accomplishments

The porphyrin monomers prepared during the previous year's work have been evaluated as sources to one- and two-dimensional solids. Reactions with a range of transition metal alkyls have provided a number of new solids, the structures of which we are presently investigating along with their catalytic potential. In addition, we have been developing the chemistry of mono-functionalized porphyrins with a view to conducting model studies of the early stages of condensation reactions with metal-alkyl bonds. Progress here is hindered by technical difficulties associated with isolation of pure mono-functionalized materials from the complex mixtures obtained in common porphyrin syntheses. A new route based on inverse micelles shows considerable promise in this regard, and we hope to obtain synthetically useful amounts of porphyrin compounds in the near future.

Numerical Treatment of Lepton Pair Production in Relativistic Heavy Ion Collisions Using Parallel Processing

Principal Investigator: Ali Belkacem

Project No.: 97004

Project Description

Electron-positron pair production will play a major role in colliders such as the Relativistic Heavy Ion Collider (RHIC) or the large hadron collider. Copious numbers of electron-positron pairs are expected to be produced at each of the interaction regions at RHIC.

Even more importantly, for each central collision, the probability for creating an electron-positron pair is unity, resulting in multiple pair production. (The probability for producing a muon pair is also high.) Because electrons and muons are expected to be used as probes for the quark-gluon plasma in case it is formed in these collisions, a good understanding and accounting of pair production from the electromagnetic process becomes critical. In addition, a sizable fraction of the electrons from the pairs produced in small-impact parameter collisions without nuclear contact are likely to be created directly bound to the ions, changing their charge states by one unit. Such ions will end up lost from the beam, becoming the main source of luminosity limitations in colliders. The capture from the pair-production process is also used at the European Organization for Nuclear Research (CERN) and Fermilab to create antihydrogen atoms.

The purpose of this project is to use the National Energy Research Scientific Computing Center's (NERSC) T3E to solve numerically the momentum-space time-dependent Dirac equation that describes the production of electron-positron pairs in relativistic heavy-ion collisions, as well as solve other atomic processes such as ionization, charge transfer, and excitation. The solution (on a grid) will give a direct visualization of the pair-creation process as the collision between the ions evolves in time. Such an approach has enormous advantages in that it provides insight through the "animation" of the collision, and also provides a powerful nonperturbative treatment for an inherently difficult problem. A great deal of experience in supercomputing and nonrelativistic scattering problems already exists. The success of our project provides a crucial first step for the extension of this expertise to the challenging and uncharted relativistic domain.

Accomplishments

After analytically constructing wave packets representing electrons and positrons, we started a first set of intensive production runs on the T3E. In these production runs, we limited the energy of the collision up to 10 GeV/n, where we have a good handle on the level of precision. The complete wave function $|\Psi(k,t)|$ containing all the information on the dynamics of the collision is calculated and stored at each time step. Similar to experimental data stored event by event, different conditions that emphasize one or another aspect of the physics are set and the

data replayed. In particular, we used the output from the T3E calculations to generate (on a desktop computer) the first animation and evolution in time of the electron density $|\Psi(k,t)|^2$. The comparison of the collision dynamic for different initial conditions, constructed from the negative and positive energy continuum states, shows the very striking behavior of the "QED vacuum" in strong fields. A rich structure is observed during the final interaction, with an apparent acceleration in the plane perpendicular to the projectile motion.

The initial wave function is "accelerated" toward the incoming projectile, afterwards spreading to include very high momenta around the center of collision (at the target site). These high momenta result from the very high fields generated by combination of target and projectile high charges. In this situation, the bound states of the combined charge "dive" into the negative-energy continuum, mixing the Dirac sea with the positive energies. The output from these runs are currently being analyzed. We performed the Fourier Transform of the momentum wave function $|\Psi(k,t)|$ at each time step to generate a time evolution of the configuration-space wave function $|\Psi(r,t)|$. The evolution of the configuration wave function gives a very clear image of the electron's motion during the interaction. In particular, we see a sharp localization of a fraction of the wavefunction around the target, which indicates that the bound-free, pair-production-transfer process is taking place.

The results of these calculations are currently being included in a paper written for publication in *Physical Review A*.

Abstracts

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Molecular Theory Group

Principal Investigators: David Chandler, Martin Head-Gordon, and William Miller

Project No.: 96030

Project Description

In this project, the Molecular Theory Group addresses the principal bottlenecks to extending molecular simulations in three interrelated areas:

- *The timescale bottleneck in molecular simulations.* Condensed-phase chemistry often occurs on timescales that are three to ten orders of magnitude longer than the nanosecond timescale of molecular simulations. Novel ways of following the crucial infrequent events that determine such reactions are required.

- *The particle number bottleneck in electronic structure calculations.* All widely used electronic-structure methods show nonlinear increases in computational cost as molecular size increases. This translates into sublinear improvements in the size of systems that can be simulated for a given improvement in computer power. The development of new linear-scaling methods is the most direct attack on this bottleneck.

- *The dimensionality bottleneck in quantum reactive scattering.* Although first-principles quantum-mechanical calculations of chemical reaction rates are now a reality for small systems, the complexity of such exact calculations grows exponentially with the number of degrees of freedom. To permit reliable treatment of larger systems, new methods that circumvent this acute dimensionality dependence are needed.

Accomplishments

Timescale Bottlenecks

In the area of timescale bottlenecks, we have developed a number of algorithms and converged on a class of techniques that solve the general problem of studying rare events in complex systems. These techniques, called "shooting," scale linearly with transition-path length. In other words, with this approach, the computational effort to harvest N transition trajectories (each one being L time steps long) is N×L. No other algorithms scale more efficiently. For example, without prior knowledge of the mechanism or transition states, we can determine 1,000 representative transition trajectories of length 1 ps with essentially the same computational effort required to simulate the same system straightforwardly for 1 ns. The straightforward trajectory simulation spends most of its time in low-energy configurations, however—encountering few if any rare events. In contrast, each of the 1,000 harvested trajectories is a statistically independent example of the rare important events.

To complement this importance sampling, we have developed and applied a battery of auxiliary techniques, including (1) a representation of reactive flux correlation functions that is especially efficient for computation from transition path ensembles; (2) quantitative criteria for knowing when transition paths are sufficiently long to be representative of the processes of interest; (3) a systematic procedure for identifying the transition-path ensemble transition states; and (4) a reversible work principle for dynamics, providing a thermodynamics for time-dependent processes, with the ability to compute time-correlation functions from methods isomorphic to thermodynamic perturbation theory. Taken together, these manifestly parallel techniques open an entirely new set of possibilities for dynamical studies of complex systems.

Particle Bottlenecks

In the area of particle bottlenecks, we have developed the first method to successfully approach linear-scaling computational complexity for systems with long-range density matrix (DM) correlations. This work involved three stages:

- Using Chebyshev polynomial expansions, we limited DM-range dependency on the system's physical properties, such as the gap between highest-occupied and lowest-unoccupied levels and temperature. Electronic structure is localized for systems with large gaps and/or high temperatures (DM correlations do not exceed the thermal de Broglie wavelength).

- We developed an efficient linear-scaling code for transforming an effective Hamiltonian into a DM via Chebyshev expansions of the Fermi-

Dirac operator. This transformation yields the DM as a finite-order matrix polynomial in the Hamiltonian, with controlled errors. Cross-overs against conventional diagonalization were established for model systems with one- and two-dimensional connectivity, using realistic tight-binding Hamiltonians.

- The method for achieving near-linear scaling DM evaluation for metallic systems, which we refer to as the Energy Renormalization Group (ERG), was developed. The ERG acts on a very hot system with a localized electronic structure, systematically cooling the temperature by a multiplicative renormalization factor. The DM is obtained as the sum of the original localized high-temperature result plus a series of increasingly nonlocal corrections resulting from each temperature renormalization. These corrections are not represented in terms of the original basis, but rather in terms of appropriate collectivized basis functions whose number diminishes exponentially with the number of renormalization steps. This exponential reduction in number occurs because the renormalization corrections do not affect the entire energy spectrum, but only an exponentially decreasing range that focuses onto the gap or Fermi level. This reduction compensates for the increase in basis function range and ensures that the entirely nonlocal DM can be represented with effort that approaches only linear growth in system size. The ERG method has been implemented on the NERSC Cray T3E, using distributed data. Near-linear scaling has been demonstrated for a one-dimensional, single-band metal—a model problem that defies existing linear-scaling methods.

Dimensionality Bottlenecks

Significant progress has been made over the last year in developing the semiclassical initial value representation (SC/IVR) to incorporate quantum effects into (otherwise classical) molecular dynamics simulations. Work is progressing along two fronts: one is the application of the SC/IVR approach to an increasingly wide range of dynamical phenomena to establish the limits of its validity, and the other is the exploration of new algorithms to make the SC/IVR calculations more efficient and thus capable of being applied to more complex molecular systems.

In one recent application, we determined vibrational energy levels of the van der Waals complex $(HCl)_2$. Although this is an anharmonic, "floppy" molecular system, the SC/IVR calculation produces energy levels in very good agreement with accurate quantum values—even describing the tunneling splitting in the ground state quite well. This work also showed how molecular symmetry is incorporated in such calculations.

In another application, we used the SC/IVR approach to calculate reactive flux correlation functions (which yield the chemical reaction rate) for a model of unimolecular isomerization in a condensed phase (a double well potential coupled to an infinite bath of harmonic oscillators). The SC/IVR treatment yielded essentially quantitative agreement with numerical quantum path integral calculations for this system. Furthermore, a linearized approximation to the full SC/IVR method worked so well that it is capable of being applied to "real" complex reactions.

Finally, a new approach was developed for evaluating the full SC-IVR flux correlation function, one that combines the two-time evolution operators in a correlation function into one semiclassical step. The "forward-backward" IVR expresses the correlation function as a single-phase space average (just as for a classical calculation) plus an integration over only a single parameter. This shows great promise for making the full SC-IVR approach only slightly more complex than an ordinary classical calculation.

Evidence is mounting, therefore, that the SC/IVR model provides a useful description of quantum effects in essentially all aspects of molecular dynamics. The appropriate (linearized) version of it is not only easy to implement (not much more difficult than ordinary classical molecular dynamics) but also adequate for many purposes. The full SC/IVR seems to be generally accurate.

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M.T. Zanni, V.S. Batista, B.J. Greenblatt, W.H. Miller, and D.M. Neumark, "Femtosecond Photoelectron Spectroscopy of the I_2^- Anion: Characterization of the $\tilde{A}'\ ^2\Pi_{g,1/2}$ Excited State," *J. Chem. Phys.* (accepted).

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Computing Sciences Division

Numerical Simulation of Turbulent Swirling Boundary Layers

Principal Investigators: John Bell and Alexandre Chorin

Project No.: 98005

Project Description

The goal of this work is to investigate the genesis, evolution, and morphology of the very intense vortical structures that arise in rotating flow, especially those in which external forces or boundary conditions lead to convergence of the rotating flow towards its axis of rotation. In most such cases, conservation of angular momentum leads to a dramatic intensification of the flow. These types of flows are observed in nature as tornadoes and are of significance in engineering applications as well. By developing a computational model based on large eddy simulation (LES) turbulence models, we hope to address some of the open questions about these structures, such as what determines the maximum windspeeds and structure of the vortex, and whether or not asymmetries and turbulence in the surrounding environment help or hinder the development and maintenance of the vortex.

Our initial effort has two main thrusts. The first was to implement and assess different LES models in an effort to select a suitable one for this type of problem. The second was to simulate axisymmetric swirling flows with an adaptive-projection algorithm so that we could investigate the dependence of flow structure and maximum windspeeds on the properties of the large-scale flow that drive the vortex.

Accomplishments

Traditionally, LES models are developed by analytically filtering the Navier-Stokes equations. The action of the filter upon the nonlinear terms in the equation generates a new term that represents the effect of unresolved scales upon the resolved scales.

Typically, the subgrid scale effects are modeled with a Smagorinsky model, which represents the local effects of turbulence with an eddy viscosity. The magnitude of the eddy viscosity in the constant Smagorinsky model is the magnitude of the local deformation tensor multiplied by an empirical constant. In the dynamic model, the eddy viscosity is computed from the flow properties as a function of space and time.

It is difficult to devise appropriate tests to quantify how accurate LES models are in modeling turbulence. One sensitive test of accuracy in turbulence modeling is to measure the anomalous dimension of a longitudinal structure function. The magnitude of a structure function scales as a power of the separation between the points being measured. If the structure function scales with the exponent predicted by the Kolmogorov theory of turbulence, the structure function is defined as having a zero anomalous dimension. In contrast, experimental measurements of turbulence reveal finite, anomalous dimensions. Our simulations of LES models with constant or dynamic Smagorinsky terms show anomalous dimensions quite close to zero. This is not surprising because the Smagorinsky term is derived from the Kolmogorov theory.

We have measured anomalous dimensions of structure functions for an LES model in which the only dissipation is provided by the Godunov finite-difference method. Interestingly, the anomalous dimensions we measured are very close to the experimental results, much more so than the results of the Smagorinsky-type LES models. This suggests that Godunov finite-difference models are a better starting point for LES models than schemes based upon a Smagorinsky term. These calculations are being repeated on much larger grids using parallel processing, in preparation for publishing this result.

We have also used the adaptive-projection methodology to perform detailed high-resolution studies of axisymmetric swirling flows representative of the near-surface flow in tornadoes and other intense atmospheric vortices. The goal of this work was to assess previous conclusions about the dependence of flow structure and maximum windspeeds on the properties on the large-scale flow that drives the vortex, but for higher Reynolds numbers and different model geometries than previously studied. We found that the previous

investigation was correct in concluding that the parameter determining the flow structure is the ratio of the far-field circulation to the eddy viscosity. Furthermore, this dependence was not affected by the geometry of the domain or by the convective forcing. We also found that the maximum windspeeds do increase with increasing Reynolds number; these higher windspeeds were not found, however, in the "low-swirl" regime as previously predicted, but rather only in the "high-swirl" regime. The results have implications for the understanding of different tornado-formation mechanisms and the maintenance of rotating and nonrotating thunderstorms.

Publications

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Parametric Visualization and Computation of Large Geochemical Data Sets

Principal Investigators: Wes Bethel, Karsten Pruess, and George Brimhall

Project No.: 98006

Project Description

Increasing computational capacity leads to increasing size and diversity of data produced by simulations. Effective use of these computational resources requires a bifurcated approach to visualization, which includes both *in situ* visualization techniques as well as techniques that accommodate heterogeneous data. *In situ* techniques operate on data while it is still resident in-core (after being computed), but without the need to transfer a large amount of data to a workstation for visualization as a post-processing step.

This project explores two heterogeneous data visualization techniques: (1) directly coupling a simulation with a visualization process on a remote workstation and (2) interactively using intuitive interfaces for data subsetting and selection. To facilitate the integration of computational models, we built a coding framework prototype that

demonstrates time-based parametric computation of geochemical data based on a first-principles mass balance model.

Accomplishments

In-Situ Volume Visualization

We developed a message passing interface (MPI) based software-parallel-volume-rendering engine with the goal of delivering five frames-per-second of direct volume rendered data from a 1024×1024×1024 dataset. Although we fell short of meeting our performance goal, we did meet the goal of direct-volume-visualization of data while it was still resident in memory, thereby obviating the need to move it to a different machine for visualization. The parallelization was performed using MPI, and the prototype tool was tested on a variety of symmetric multiprocessor (SMP) and distributed-memory architectures. This work will be integrated into other visualization tools for use by the National Energy Research Scientific Computing Center (NERSC) and LBNL community, such as those produced by the Center for Computational Science and Engineering (CCSE) at NERSC. Figure 1 is an image of combustion data produced by a simulation run on a NERSC supercomputer.
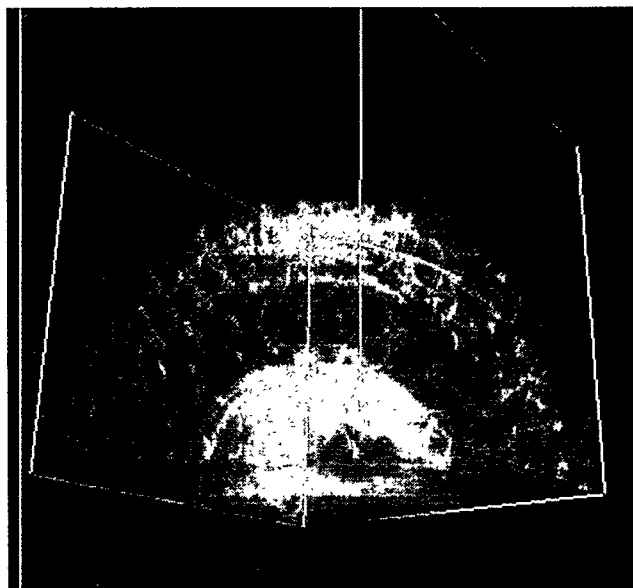
Figure 1. Image of combustion data produced by simulation run on NERSC supercomputer.

Multi-Resolution Visualization and Intuitive Interfaces for Data Subsetting

As an alternative approach for large data visualization (faster tools for visualizing large amounts of data), we developed a set of prototype tools that permit the user to perform interactive subsetting of large data sets (Figure 2). A reduced-resolution version of a data set is presented to a user (Figure 3), and then the subset of data is processed with full-resolution visualization tools (Figure 4).
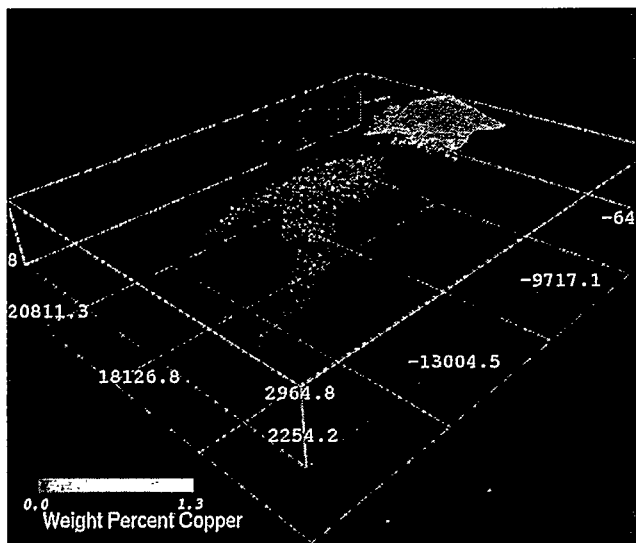
Figure 2. *Interactive subsetting of large data sets.*
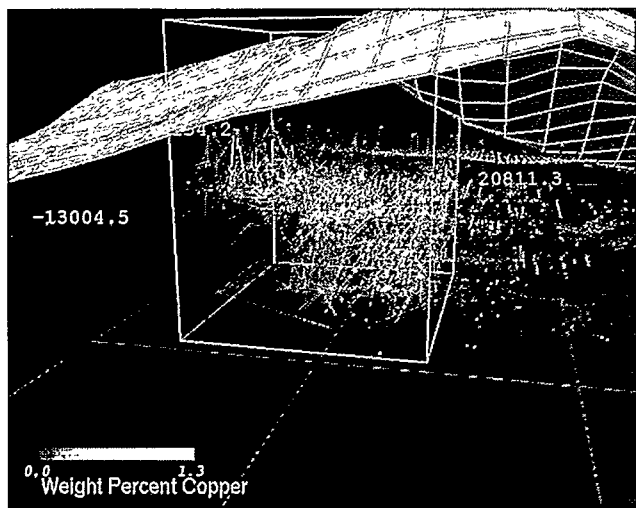
Figure 3. *Reduced-resolution version of data set.*
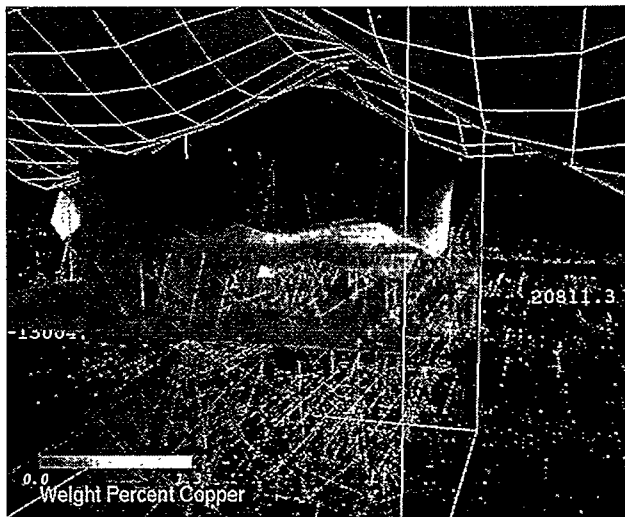
Figure 4. *Subset of data processed with full-resolution visualization tools.*

Coupling Simulations with Remote Visualization Tools

We developed a software library that may be used to instrument a simulation, thereby coupling the simulation with a remotely executing visualization tool. Source code for this tool is located at http://vis.lbl.gov/projects/fy98_ldrd.bethel/dblaster.tgz. This tool implements a client-server model for communication using sockets and uses XDR for conversion of floating-point formats between different architectures. XDR, an acronym for eXternal Data Representation, is used for architecture-independent storage and transmission of data across digital networks. Figure 5 shows the results of a
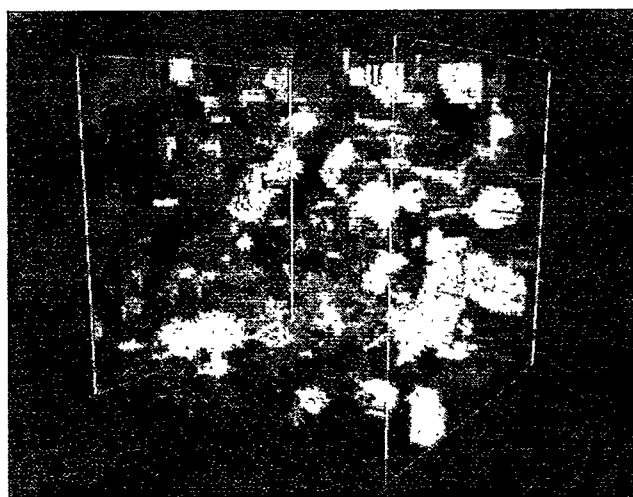
Figure 5. *Results of lattice-gauge simulation run of large NERSC supercomputer.*

lattice-gauge simulation run on a large NERSC supercomputer, transmitted to and then visualized on a desktop workstation.

Time-Based Parametric Computation and Visualization

The coding prototype models the effects of rainwater entering the system from the ground level (the topmost surface in Figure 6) and migrating downward, thereby displacing copper from an "enrichment blanket" layer. The copper then migrates further downward into a protore layer. Our model assumes downward travel only. Further work would incorporate lateral motion and reactive chemistry modeling.
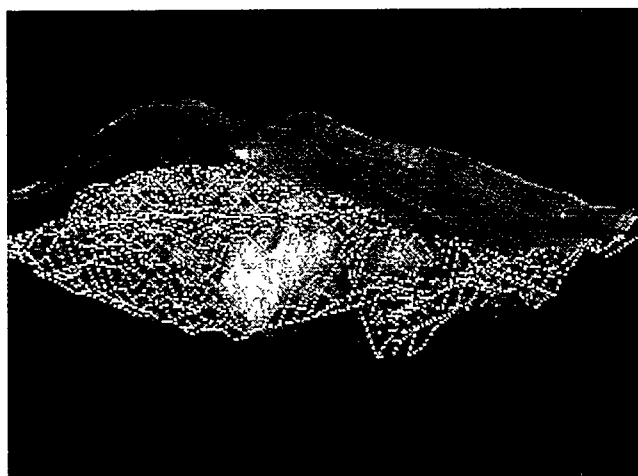
Figure 6. Coding prototype modeling the effects of rainwater entering the system from the ground level (the topmost brown surface).

Publications

W. Bethel, V. Beckner, and T. Ligocki, "Fast Volume Visualization from Composited Two-Pass Affine Image Transformations," LBNL-41587 (submitted to IEEE SC98 and Visualization 98).

Numerical Methods for Time-Dependent Viscoelastic Flows

Principal Investigators: Alexandre Chorin and Raz Kupferman

Project No.: 98007

Project Description

Many liquids of technological significance are viscoelastic in that the stress state depends on the history of the deformation. (The stress in common liquids like water and glycerine depends only on the instantaneous rate of deformation.) Polymeric materials are typically processed in the melt, where much of the molecular orientation that determines solid-state properties is developed; the viscoelasticity of molten polymers is a major factor in the shaping of materials and development of structure in molds and extrusion dies. Polymeric materials are being increasingly used in transportation and will be a major component of any successful lightweight vehicle design.

Viscoelastic liquids exhibit instabilities that are not observed in low-molecular-weight liquids, and such instabilities are often the limiting factor in fabrication processes. Simulation of flow of viscoelastic liquids has been an active area of research for two decades, motivated by the need to develop practical schemes for analyzing flow and structure development in processes such as injection molding. Disappointingly-slow progress has been documented in reports from a series of biennial workshops, the tenth of which will be held this year. Though commercial codes are available, numerical schemes for viscoelastic liquids are still inadequate to describe steady processing flows in regimes of technological importance, where the outstanding issue is the development of robust schemes for flows with large stress gradients, and the existing codes are not useful for the practical analysis of extrusion and molding operations. Little has been done to describe transient flows, with the notable exception of work by D.D. Joseph and coworkers on the motion of falling particles in viscoelastic liquids.

The focus of our project has been the development of efficient computational methods for high-Reynolds number flow of Newtonian fluids. New approaches to numerical simulation of the flow of technologically

interesting non-Newtonian fluids are badly needed; methods currently in use are inefficient and fail to converge for parameter ranges of technological significance. We will explore the applicability of advanced computational techniques developed in our program to viscoelastic fluids of interest to investigators in the Materials Sciences Division (MSD), with emphasis on flows being experimentally studied by MSD investigators. If we are successful, the new method will significantly change the practice of numerically simulating viscoelastic fluids.

Accomplishments

We recently developed a new family of numerical schemes for flow equations based on second-order finite differencing with the projection method. This family of schemes is a second-order extension of the Lax-Friedrichs scheme. Based on the Godunov paradigm, the solution at each time step is initially interpreted as representing cell-averages, which are then (1) approximated by a piecewise-polynomial function that is evolved in time and (2) averaged over the computational cells. In the central difference framework, these averages are calculated over a staggered grid rather than over the same computational cells used to construct the piecewise-polynomial approximation. As a result, the entire characteristic fan emanating from the discontinuous breakpoints is integrated, and no Riemann solver is necessary. The simplicity of treatment of the hyperbolic operator makes this scheme particularly suitable for more complicated dynamics such as those found in viscoelastic flow.

We tested the new scheme on the canonical problem of the periodic double shear-layer. Although the scheme proved to be slightly inferior to upwind schemes in terms of accuracy and resolution, it was more robust and immune to the formation of the spurious structures that typically form when the flow is under-resolved. Its primary advantages of simplicity and generalizability were demonstrated when we solved the Couette-Taylor problem for a Newtonian fluid using cylindrical coordinates. We explained how to extend the method to cope with general systems of coordinates and boundary conditions. The generalization to viscoelastic fluids and more complicated flows appears to be within reach, opening a new field of computations.

We will test extension of the new numerical scheme to the transient flow of viscoelastic fluids described by differential constitutive equations, with a goal of describing the transition to flow instabilities that have

been observed in viscoelastic liquids but not in Newtonian fluids. The viscoelastic model developed by Giesekus will be used initially, in which stress is related to the deformation rate through the following equation:

$$\frac{\partial \sigma}{\partial t} = -(u \cdot \nabla)\sigma + (\nabla u)^\dagger \cdot \sigma + \sigma \cdot (\nabla u)$$
$$- \frac{1}{\lambda}\sigma + 2\frac{v_p}{\lambda}D - \frac{\alpha}{v_p}\sigma^2$$

In its assumption that the fluid is characterized by a single stress relaxation time, this equation is an approximation of the behavior of real polymeric fluids, but it also generally represents important aspects of the rheological response of polymer solutions and melts. We will test the approach in flows with large stress gradients for which reliable numerical solutions have not been achievable until now—both to predict regions where flow instabilities unique to viscoelastic materials may occur and to determine whether reasonably steady states can be approached in stable regimes. This study will complement an experimental program being carried out by S. Muller in MSD on the onset of Couette-Taylor instability in polymer solutions, where viscoelasticity has a major impact on the onset and form of the transition as well as on the onset of unstable flow between rotating plates and cone-plate systems used for rheological measurement. The apparent sensitivity of the Couette-Taylor transition to the rheological properties of the polymer makes the former flow an excellent test of both constitutive theories and numerical methods. Because the latter flows are central to the characterization of the stress state of polymeric fluids, it is crucial to understand these still-unexplained experimentally-observed instabilities.

Publications

R. Kupferman, "A Numerical Study of the Axisymmetric Couette-Taylor Problem Using a Fast High-Resolution Second-Order Central Scheme," LBNL-40036 (February 1997).

Integration of PDSF, HENP Analysis, and HPSS Data Archive

Principal Investigators: Craig Tull, Jason Lee, Brian Tierney, Wayne Hulbert, William Kramer, Keith Fitzgerald, and Doug Olson

Project No.: 97033

Project Description

The goal of this project was to provide a consistent set of improvements to the underlying infrastructure for High Energy and Nuclear Physics (HENP) computing facilities. HENP computing activities for large experiments are geographically distributed as a result of (1) the size of the collaborations and the scale of the manpower effort for software development and data analysis and (2) the hardware resources needed to cover the entire range of computing needs. This project developed and implemented an architecture that satisfies these requirements, in that it (1) applies the capabilities of NERSC in playing a key role for certain classes of computing needs (i.e., simulations, analysis, and data management) and (2) satisfies the global scope of computing for HENP.

Accomplishments

This project:

- Developed, demonstrated, and characterized a software-based architecture that supports a high-volume, distributed, data-intensive computing environment to support HENP data handling and analysis.

- Provided a prototype-production HENP computing environment that integrates PDSF, a high-speed data cache, and archival storage within the NERSC environment.

The overall approach was to augment and utilize the characteristics of several existing systems (Particle Data Storage Facility (PDSF), Distributed-Parallel Storage System (DPSS), and High Performance Storage System (HPSS)), to provide the elements of the high throughput data handling and analysis architecture, and then to design and build the interfaces and data movement managers that will provide overall high-speed data movement and management among the systems. The Standard

Analysis Framework (StAF) was used to provide the prototype analysis code to validate and characterize the architecture and implementation.

Our project had three components

- *Integrate the DPSS with the PDSF.* To expand the availability of the DPSS environment, integration with the PDSF is essential because most of the HENP client community do their simulation and analysis work there. This work required porting software and a network interface between the 10 Mbps PDSF Ethernet and 100 Mbps DPSS Ethernet.

- *Integrate the DPSS with the HPSS.* The DPSS provides a high-speed, low-cost disk cache. The data volume for HENP exceeds the DPSS capacity, so it is necessary to integrate the DPSS to an archival storage system. The NERSC HPSS system is designed for such integration. The LDRD program funded additional network-based interfaces for the HPSS bitfile movers (to allow high-speed network access to the HPSS) as well as the design and software development to accomplish the integration.

- *Performance evaluation of HENP workloads.* This workload includes both the simulation (event generation and detector response) and event analysis: two components with different computational requirements.

Integration

When this work began, PDSF, DPSS, and HPSS were independent systems, connected only with common network methods such as Transmission Control Protocol (TCP)/Internet Protocol (IP), File Transfer Protocol (FTP), and telnet. The logical diagram of these systems is shown Figure 1.

The process of integration needed to accomplish two things. First, the DPSS and HPSS were integrated, essentially replacing the HPSS disk cache with DPSS. This allowed very fast random access to the data from multiple clients simultaneously and higher access speeds to the HPSS than with standard FTP. The DPSS API was then integrated into StAF, thereby hiding the specifics of the DPSS interface from most physics applications.

The project goal was to create and evaluate the performance of a system (see Figure 2) that is logically designed to provide high bandwidth archive storage for HENP applications.
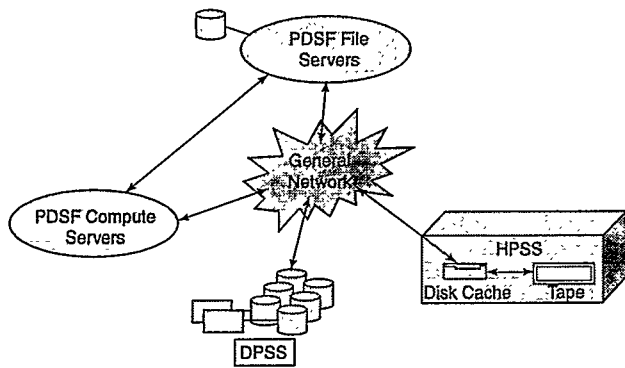
Figure 1. There were four separate systems when our work started, connected with low-speed commodity network interfaces.

Empirically, the average input/output (I/O) bandwidth seen between the PDSF and HPSS with the old (i.e., 100 Mb/sec backbone bottleneck) network configuration was dependent on the HPSS class of service (COS). The same is true for the I/O bandwidth seen with the new network connection (i.e., 400 Mb/sec direct connection). In production simulation runs conducted by STAR experimenters reading data with parallel FTP (pftp) from HPSS large file-size COS, an average I/O rate of 2.25 Mb/sec was typical with the old network connection, while rates as high as 5.75 Mb/sec were seen using pftp from HPSS medium file-size COS.

With the new network configuration between the PDSF and HPSS, pftp transfers between PDSF and HPSS medium file-size COS are summarized below:

- Single transfer from HPSS medium file-size COS: 4.91 Mb/sec.

- Single transfer to HPSS medium file-size COS: 3.57 Mb/sec.
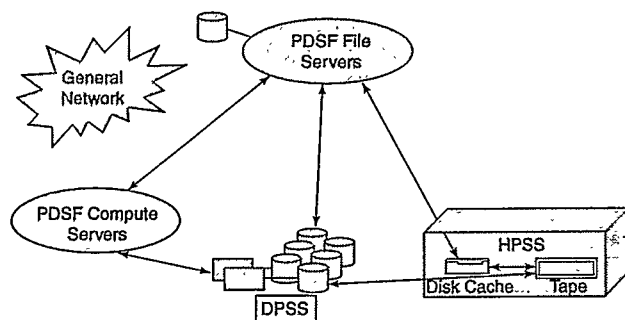
Figure 2. At completion of our work, there was one integrated set of systems connected with high-speed network interfaces.

- Two simultaneous transfers from HPSS medium file-size COS on single bit-file mover: 6.23 Mb/sec.

- Two simultaneous transfers from HPSS medium file-size COS on two separate bit-file movers: 9.64 Mb/sec.

Impact

The impact of this project is significant. First, the fact that the DPSS was integrated easily with the PDSF using StAF demonstrated the value of using modular well-engineered software. The work resulted in the integration and test of research software into a production computing environment with no interruption of service.

Second, the integrated system provided enhanced functionality by giving the PDSF a very large storage capacity with cost-effective, high-speed disk caching. This added functionality was achieved with no loss of performance or service.

Third, by using the DPSS integrated with computational systems, this project demonstrated that HENP applications can achieve 35 Mb/sec I/O performance—several times what had been achieved to the HPSS or local disk in the old configuration.

The results of this project are being considered for permanent support within the PDSF production system. The PDSF continues to expand and attract new customers. In part as a result of this project, funds to upgrade the PDSF were acquired from several sources, and the entire complex of systems was replaced with new systems at the end of FY98.

This project was also part of the groundwork for the successful "China Clipper" proposal funding in FY99.

Accurate Segmentation of Cells with Level Set Methods

Principal Investigator: Ravi Malladi

Project No.: 98008

Project Description

The aim of this project is to develop algorithms for confocal microscope image analysis that are based on level set techniques. The geometric techniques we

adopt were originally designed for extracting tumor volumes and organ shapes from medical images.

The motivation for using these techniques in computer-aided cytology is derived from a number of observations. For a wide variety of solid tumors, clinical pathology shows increasing spatial disorganization of cells in tissue specimens and increasingly abnormal structural features of the individual cells as carcinogenesis progresses from apparently normal cells to cancer. Although pathology enables disease staging and treatment planning, it does not reveal the underlying molecular mechanisms driving the disease process. Understanding these mechanisms is essential for improving cancer prevention and developing new therapies targeted at an individual's disease (e.g., gene therapy).

A powerful approach for gaining insight about underlying disease mechanisms is to combine standard pathology with techniques that quantify specific molecular species in individual cells. Techniques for this approach involve immunocytochemistry and fluorescence *in-situ* hybridization for labeling the molecules of interest. Quantitative information is extracted by first applying this technique to thick (20-µm) tissue sections where intact cells are present for analysis. The tissue sample is then imaged through a 3D (confocal) microscope followed by 3D image analysis. For all measurements, the image-analysis algorithms must identify individual cells within tumor tissue and accurately delineate the boundary of identified cells and their nuclei.

Accomplishments

Our collaborators, S. Lockett and C. Ortiz de Solorzano at LBNL's Life Sciences Division, have recently completed a computer program for segmenting the individual, fluorescence-labeled cell nuclei inside intact, thick tissue. It correctly segments a large percentage of the nuclei based on visual judgment and is now being used to study the structural reorganization of the nucleus during tumorigenesis. Applications would benefit from improved segmentation, and an alternative, noise-insensitive segmentation method based on the Hough Transform has been demonstrated, which combines edge information from the image with *a priori* shape information in a procedure to shrink and thus separate nuclei. It identifies a greater proportion of individual nuclei than our current method, but its utility is limited by imprecise surfaces when two

nuclei touch. In the past six-to-nine months with the current LDRD funding, we have shown that denoising and shape recovery of the images lead to more efficient and accurate segmentation of the nuclei. In particular, we have used partial-differential-equation (PDE) based, geometry-driven, image-enhancing procedures as a preprocessing step. We have also demonstrated that procedures adding to the accuracy of the final segmentation (like hole removal and cluster reclassification) can also be done within the PDE framework, using variations of our basic model. Figure 1(a)-(b) shows the result of solving an edge-preserving denoising procedure on a 3D confocal microscope image, and 1(c)-(b) shows the result of our shape refinement and declustering algorithm.

(a)   (b)

(c)   (d)
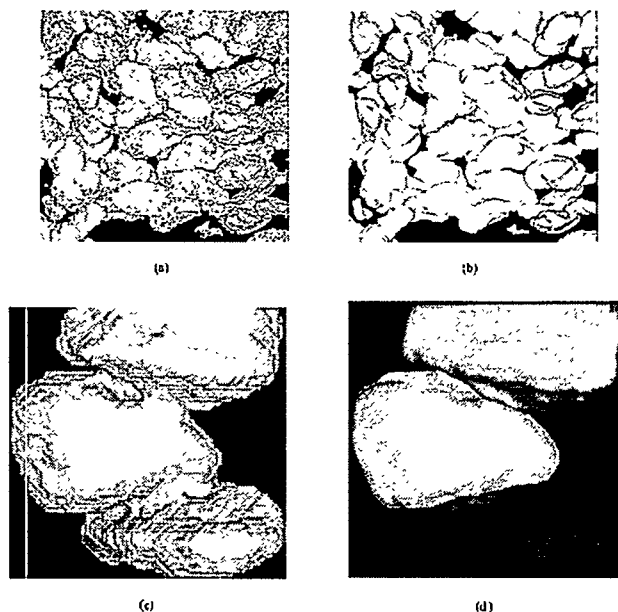
Figure 1. Geometric partial-differential-equation-based methods for confocal image analysis: (a)–(b) denoising a 3D image using geometric methods, (c)–(d) shape refinements and declustering result.

Publications

C. Ortiz, A. Sarti, E. Garcia Rodriguez, A. Jones, D. Sudar, D. Pinkel, J. W. Gray, and S. J. Lockett, and R. Malladi, "Segmentation of Cell Nuclei from Confocal Microscope Images of Thick Tissue Samples," Proceedings of the Fourth Joint Conference on Information Sciences, Research Triangle Park, North Carolina (Oct. 23–28, 1998).

A. Sarti, C. Ortiz, S. Lockett, and R. Malladi, "A Unified Geometric Model for 3D Confocal Image Analysis in Cytology," Proceedings of SIBGRAPI'98:

International Symposium on Computer Graphics, Image Processing, and Vision, Rio de Janeiro, Brazil (Oct. 20–23, 1998).

Electron Collisions with Molecules, Clusters, and Surfaces

Principal Investigators: C. William McCurdy and Thomas Rescigno

Project No.: 96043

Project Description

Electron collisions, with a variety of different species and in a variety of environments, play a key role in plasma etching and deposition processes as well as in a number of waste remediation processes currently under development at DOE laboratories. Relatively little is known about such collisions, despite the important role they play in surface characterization, plasma-wall interaction, electron-induced desorption, and reorganization of adsorbed particles. Although the past few years have witnessed tremendous progress in the development of sophisticated *ab initio* methods for treating collisions of slow electrons with isolated small molecules, the practical need to study electron collisions with the complex molecules and fragments encountered in real-world plasma processing environments, as well as with molecules in complex environments (e.g., at interfaces, on surfaces, or in clusters), taxes present methods far beyond their current capabilities.

The purpose of this research is to develop theoretical and computational tools for treating electron and photon interactions with targets that are presently beyond the grasp of *ab initio* methods. We want to develop new methods for dealing with heavier molecules, complex molecular clusters, and (ultimately) molecules bound to surfaces and interfaces. Moreover, we want to extend our capabilities to intermediate energies from the ionization threshold to a few hundred eV—a region that presents a formidable challenge for *ab initio* theory.

The approach will build on our unique capabilities, based on the complex Kohn variational method for calculating cross sections for gas-phase electron scattering (elastic, vibrational excitation, electronic excitation, dissociation, and attachment) and photoionization processes involving small polyatomic molecules. The formalism will be extended to include pseudopotential methods, complex optical potential interactions, and scattered flux operator techniques.

Accomplishments

The activities covered by this project have been characterized by two common themes. The first is a need to develop practical computational methods for treating complex polyatomic targets and molecules found in real-world plasma environments. For many of the feedstock gases used in these industrial plasmas, there are little or no experimental electron-impact cross-section data available; thus, theory is the sole source of critically needed collision data. With the continued theoretical and computational improvements to the methods we have been developing under this project, we have been able to increase the complexity of the target gases we can study. We completed and published a theoretical study of low-energy electron scattering by BCl_3, a gas that is widely used in the plasma etching of silicon and for which little experimental data presently exist. Some of these data are depicted in Figure 1. We have also initiated a study of low-energy electron scattering by CO_2.

The other theme this project addresses is the need for practical schemes to calculate cross sections in energy regions characterized by a dense level of excited states, including ionization continua. We have continued to make significant progress on developing practical methods to study electron-impact ionization. The key feature of the approach we are developing is that it uses flux operators to extract both total and singly differential (energy-sharing) ionization cross sections from a scattered wave function that is constructed without explicit imposition of asymptotic ionization boundary conditions. Initial tests of these ideas had been carried out for electron-hydrogen atom scattering in the standard spherical model. We have moved beyond the model problem to a treatment of the full three-body Coulomb problem with no approximations, a problem never previously solved. Our approach requires the iterative solution of very large (several million by several million) systems of complex linear equations, for which the full resources of the Cray T3E are being used.
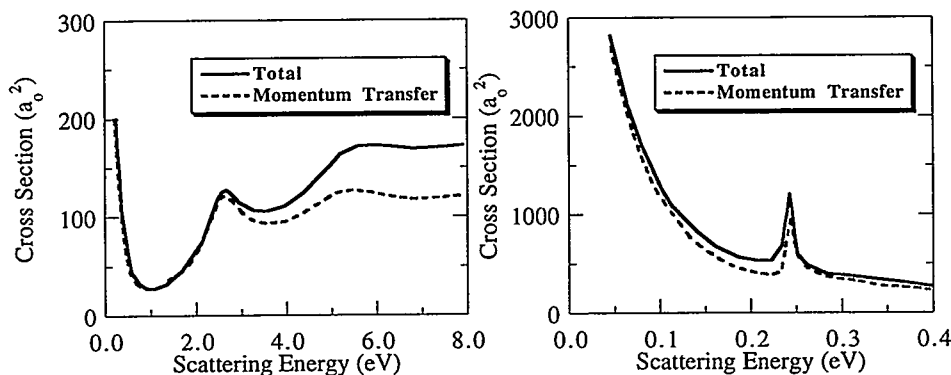
Figure 1. Low-energy e-BCl$_3$ scattering cross sections. Left: total elastic and momentum transfer cross sections; right: cross section detail below 0.4 eV, showing a narrow B$_2$ shape resonance feature against a rising, virtual state enhanced background
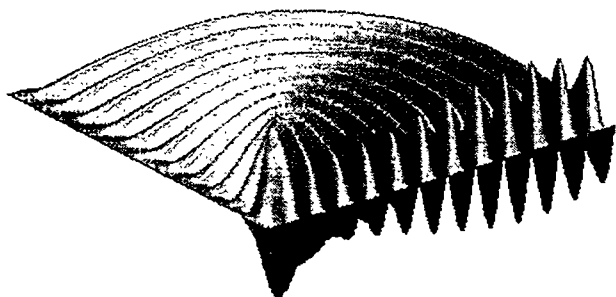
Figure 2. A sample partial-wave component of the full e-H wave function. The peaks along the right edge correspond to excitation of the hydrogen atom. The outgoing waves represent ionization flux.

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Scientific Computing on Clusters of Multiprocessor Systems (COMPS)

Principal Investigator: William Saphir

Project No.: 96037

Project Description

Scientific computing relies increasingly on hardware developed originally for nonscientific applications. The days of expensive special-purpose hardware are nearly over, as scientists rely more than ever on commodity and near-commodity equipment. On the low end, scientific computing uses workstations or PCs and (to a lesser extent) symmetric multiprocessor (SMP) servers, usually with fewer than ten processors. On the high end, the fastest scientific computers are massively parallel processors (MPPs), which are based on commodity microprocessors and look to the programmer like a tightly integrated collection of single-processor workstations. MPPs use

specialized network hardware. Increasingly, high-end computers are being built from commodity hardware, including commodity network hardware.

The premise of this project is that the next important architecture for scientific computing will be clusters of multiprocessor systems (COMPS) connected by commodity networks. SMP clusters, which incorporate aspects of the current high and low end, have the advantages of low cost (because of their commodity-base scalability) and flexibility (because they are distributed).

SMP clusters present a number of challenges that must be addressed by applications and system software. COMPS LDRD research addresses a range of issues that need to be understood before SMP clusters can be used effectively. It is not even clear, for instance, what the programming model should be, because several combinations of message passing, explicit threads, and compiler parallelization are possible. Process scheduling and networking software are more complex and more critical for performance than for traditional MPPs.

The COMPS LDRD is looking simultaneously at system-software and application-software issues. The application areas—primarily numerical computation but also data-intensive computing and experiment control—serve as drivers for selecting important computing technology areas. System software work includes both evaluation of existing technology, such as the NOW (network of workstations) software developed at UC Berkeley, and development of technology where it does not already exist.

Accomplishments

The premise of the COMPS LDRD, which began in 1996, has proven to be correct: SMP clusters are just about to become the dominant architecture for high-performance computing. Indeed, the high-end machines available in the time frame of the NERSC-3 and possible Strategic Simulation Initiative procurements are almost exclusively SMP clusters. The experience gained in the COMPS project, particularly in the areas of programming paradigms and implementation of communication subsystems, is being directly applied to the NERSC-3 effort.

A second major accomplishment of the COMPS LDRD is the development of M-VIA, a modular implementation of the virtual interface architecture (VIA) standard for Linux. M-VIA provides high-performance interprocess communication on SMP clusters. It has had a significant impact on the

definition and clarification of the standard and has attracted interest from dozens of companies, government labs, and universities. M-VIA forms the basis of a proposed Cooperative Research and Development Agreement with Intel that has been submitted to the Department of Energy Laboratory Technology Research program for funding.

COMPS application research has led to the development of parallel genetic algorithm software that will be used by M. Van Hove and collaborators in the Materials Science Division. This work will lead to one masters degree: G. Stone, "A Scalable Genetic Algorithm Package for Global Optimization Problems with Expensive Objective Functions," San Francisco State University.

In this latter portion of the project, the researchers addressed the global optimization problem. The solution of complex structures is the primary remaining difficulty for low-energy electron diffraction (LEED) and many other surface structural techniques. Steepest-descent methods can find only a locally optimum structure; a global search is required to find the globally optimum structure. A promising approach is that of genetic algorithms, which have been effective in a wide variety of optimization problems. The excellent results of an earlier study applied to a relatively simple structure have led us to explore the capabilities of genetic algorithms for more challenging problems. The genetic algorithm approach is ideally suited to parallel computing and is being developed on a particular type of NOW.

Publications

M. Van Hove, "Global Optimization in Materials Sciences with Parallel Genetic Algorithms," DOE Workshop on Mathematical Aspects of Materials Sciences Modeling, Gatlinburg, Tennessee (April 28, 1998). For corresponding slide presentation, see http://electron.lbl.gov/leed/gatalk/gatalk.html.

Sparse Linear Algebra Algorithms for Massively Parallel Processors (MPPs)

Principal Investigators: Horst Simon, Beresford Parlett, and James Demmel

Project No.: 97026

Project Description

Our goal was to develop scalable parallel algorithms to solve large sparse symmetric, indefinite eigenproblems. No general purpose, library-quality solver exists on distributed memory machines. Our research addressed several crucial issues for large-scale parallel machines, such as robustness, scalability, and portability. Although our development is mainly on the NERSC T3E, we used machine-independent software environments such as Fortran and C with message passage interfaces (MPI). The resulting algorithm library is easily portable to other platforms and emerging achitectures. Our new algorithms will enable the efficient solution of common problems arising in computational chemistry, physics, and material sciences.

Accomplishments

We ported and parallelized the scalar LANSO code by B. Parlett, which runs efficiently on the Cray T3E 512 processor and demonstrates very good speed-up. The ability of the code to be implemented in MPI and portable to other platforms has been demonstrated on the symmetric multiprocessor (SMP) cluster of multi-processor systems. On this cluster, we also studied the trade-off between shared memory (threads) and distributed memory (MPI) parallelism.

In the process of comparing our PLANSO code to the PARPACK software from Rice University, we found that PLANSO runs consistently faster than PARPACK. In addition to the inherent higher efficiency of the Lanczos algorithm, this increased speed is due to a new algorithmic technique called "thick restart" (TRLAN). With thick restart, the Lanczos algorithm has the same advantage of reduced storage as PARPACK. Implementation of the TRLAN package is complete, and the software has been made available to a number of users. In particular, we successfully collaborated with a NERSC user in the materials sciences community,
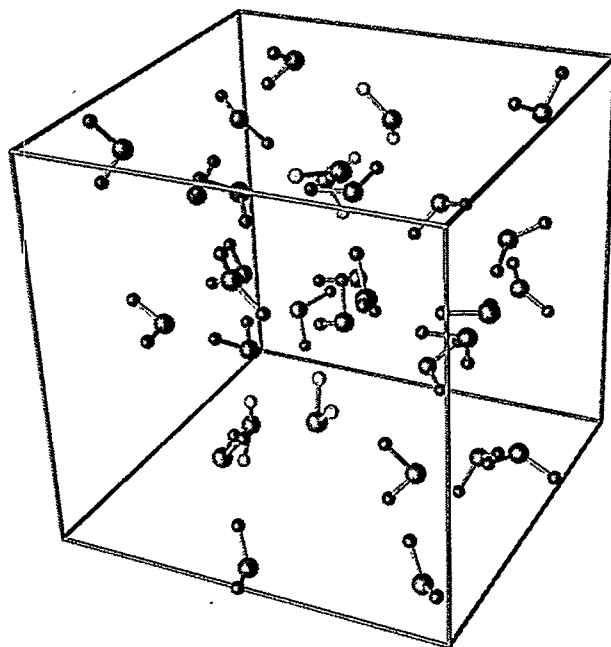
Figure 1. This configuration of molecules in liquid water is used in an ab initio computation of nuclear magnetic resonance chemical shifts. Materials science applications such as this will benefit from improved scalable sparse linear algebra algorithms.

who is using this algorithm now. Other applications (e.g., to the partitioning problem) are under investigation in collaboration with A. Sohn.

We investigated four applications of the Lanczos algorithm:

- First, we continued investigating the Lanczos algorithm and its use in solving the problem of large text retrieval in latent semantic indexing (LSI). In our theoretical work, we demonstrated the advantages of Lanczos-based LSI as well as corrected an error in the published literature on this topic. In collaboration with the Web search engine Inktomi (Hot Bot), we computed the first five singular values of a 100,000 terms by 2,559,430 documents data matrix using our algorithm. We believe that this is the first time the singular value decomposition (SVD) of such a large matrix has ever been computed. Three followup reports on improved algorithmic techniques were published in FY98, including the application of specialized algorithmic techniques for dealing with the structure of the spectrum of LSI matrices.

- Second, we collaborated with D. Vasco in the Earth Sciences Division, using our algorithms to solve inverse problems arising in the study of the earth's interior structure. The resulting matrices were of the order: 1.5×10^6 by 2×10^5.

- Third, we considered application of the new Lanczos algorithm in electronic structure calculations in the Cohen-Louie materials sciences group at UC Berkeley. In this case, direct application of the Lanczos code proved to be less effective than a conjugate-gradient minimization.

- Fourth, we continued our collaboration with Boeing, where J. Lewis and R. Grimes have been working on a related project. Boeing has released the SPOOLS software to NERSC, a sparse symmetric, indefinite solver that is currently being evaluated and tested.

The principal investigators would like to acknowledge the following collaborators: John Wu (NERSC), Osni Marques (NERSC), Hongyuan Zha (Pennsylvania State University), Don Gehring (UC Berkeley), and Xiaohui Wang (Pennsylvania State University). Other collaborators on the project were Steve Barnard (NASA Ames Research Center), John Lewis (Boeing, Seattle), Michael Palmer (Inktomi), Bernd Pfrommer (Sun Microsystems), and Andrew Sohn (New Jersey Institute of Technology).

Publications

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A. Sohn and H. Simon, "SHARP: A Parallel Dynamics Spectral Partitioner," Proceedings of IEEE SC '98, Orlando, Florida (1998).

X. Wang and H. Zha, "An Implicitly Restarted Bidiagonal Lanczos Method for Large Scale Singular Value Problems," LBNL-424472 (August 1998).

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H. Zha and H. Simon, "On Updating Problems in Latent Semantic Indexing," CSE Tech. Report CSE-97-011, 1997 (accepted for publication in *SIAM J. Matrix Analysis and Applications*, 1999).

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H. Zha and Z. Zhang, "On Matrices with Low-Rank-Plus-Shift Structure: Partial SVD and Latent Semantic Indexing," LBNL-42279 (August 1998).

Earth Sciences Division

Effect of Biosorption on Actinide Migration in Subsurface

Principal Investigators: Ilham Al Mahamid and Jennie Hunter-Cevera

Project No.: 97007

Project Description

The presence of actinides in radioactive waste is a major environmental concern because of their long radioactive half-lives, their highly energetic emissions, and their chemical toxicity. Remediation of actinides requires stabilization or removal; they cannot be degraded like organic contaminants.

This work focuses on the interaction of actinides with microbial soil in the presence and absence of organic chelating agents. Microorganisms can accumulate actinides, leading to either a slower or a faster rate of transport, depending on the mobility of the microbial population. We selected ethylenediaminetetra acetic acid (EDTA), a significant contaminant present in actinide waste, as a chelating agent for plutonium (Pu). (The biosorption of neptunium, americium, and plutonium by several microorganisms was reported earlier.)

Accomplishments

We investigated the biosorption of actinide on several metabolically inactive microorganisms. These microorganisms were selected for their ability to degrade organic components of mixed wastes or for their environmental relevance. The microorganisms (provided by W.T. Stringfellow) were *Pseudomonas aeruginosa* NRRL B-4452 (heavy metal uptake strain), *Pseudomonas aeruginosa* CV1 (phenol degrader from refinery), *Rhodococcus erythropolis* GOMEX2 and *Pseudomonas stutzeri* P-16 (PAH degraders), *Gordona bronchialis* RR2 and *Rhodococcus rhodochrous* RR1 (toluene degraders), *Mycobacterium parafortuitum* ATCC19686 and *Micrococcus luteus* (common gram-positive), and *Pseudomonas fluorescens* and *Acinetobacter sp.* (common gram-negative).

We then conducted a comparison study of chelated and unchelated plutonium biosorption. Studies were carried out in batch experiments under argon atmosphere. The unchelated Pu tested was Pu(III), and the chelated Pu was Pu(IV)-EDTA. Results presented in Figures 1 and 2 show that the
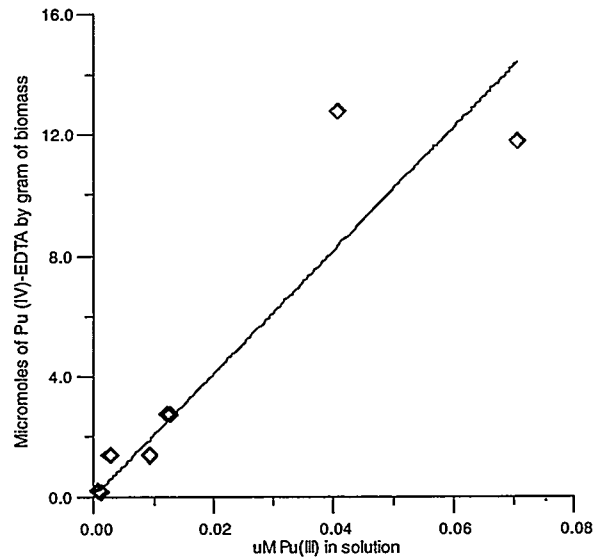
Figure 1. *Sorption of Pu(III) by Ps. aeruginosa B4452.*
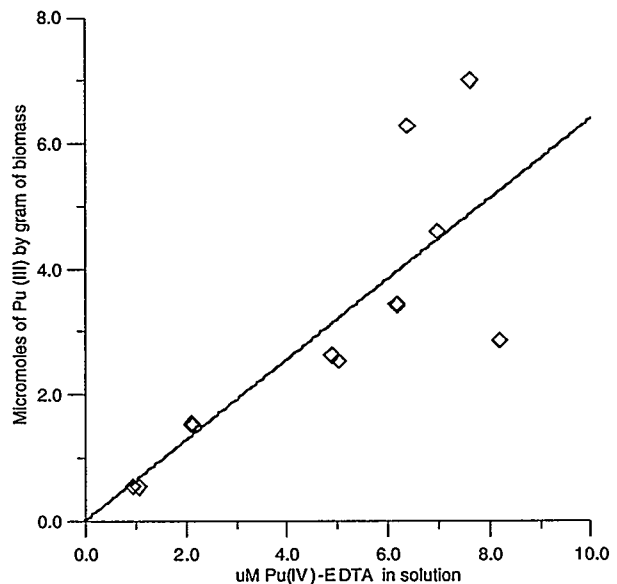
Figure 2. *Sorption of Pu(IV)EDTA by Ps. aeruginosa B4452.*

biosorption of unchelated Pu is significantly higher than that of the chelated Pu.

Publications

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Ocean Particulate Carbon Dynamics

Principal Investigator: James Bishop

Project No.: 98035

Project Description

There is an urgent need to devise strategies to stabilize the levels of carbon dioxide in the atmosphere. The purpose of this project is to carry out fundamental research into the dynamics of particulate carbon off the coast of California. The sedimentation of particulate organic carbon is the ultimate burial of atmospheric carbon, but particulate carbon dynamics is not well understood because of the difficulty and exorbitance of direct high-precision measurements of trace constituents in the water column. This project seeks to explore the development of an economical autonomous device that profiles particulate organic carbon (POC) concentration in the water column on time scales fast enough (~diurnal) to capture biological variability. The device will be cheap enough to permit the first large-scale quantification of the geographic and temporal distribution of POC. We will also analyze existing samples of particulate matter from the North Pacific and other environments for compositional information that may yield insight into the processes of formation and removal of particulate carbon.

Accomplishments

One of the major thrusts of our proposal is to develop methodology for autonomous monitoring of carbon system parameters in the oceanic water column.

With the initial four months of funding, we have built collaborative relationships among J. Bishop (chemical oceanography, particulate matter dynamics), R. Davis (ocean engineering/physical oceanography at Scripps), G. Mitchell (remote sensing biology at Scripps), C. Moore and R. Zaneveld (inherent ocean optics technology at WETLABS Inc.), and J. Morrow and R. Booth (apparent ocean optics technology at Biospherical Instruments). The team is working to implement carbon system sensors on the SOLO float, a second generation autonomous profiling float developed at Scripps Institute of Oceanography (SIO), and on the autonomous navigated underwater glider (Spray) under joint development by SIO and Woods Hole Oceanographic Institution (WHOI). These are capable, respectively, of 150 and 600 profiles to 1000 m, providing, e.g., twice daily sampling for 2.5 and 10 months. Spray, which can navigate against currents, should be particularly useful for work in continental shelf and slope waters. Our group at LBNL has shown that marine organic carbon biomass may be quantified accurately and precisely using a fixed wavelength transmissometer. We expect to develop optical methods to quantify particulate inorganic carbon as well as other carbon system parameters. Biospherical Instruments and WETLABS will implement improved sensors on the autonomous platforms. The team hopes to obtain support for these efforts under the National Oceanic Partnership Program.

Also supported under LDRD funding is workup and publication of data and samples on particulate matter dynamics collected during four oceanographic cruises to the subarctic northeastern Pacific Ocean during 1996 and 1997.

Publications

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P.W. Boyd, N.D. Sherry, J.A. Barges, J.K.B. Bishop, S.E. Calvert, M.A. Charette, S.J. Giovannoni, R. Goldblatt, P.J. Harrison, S.B. Moran, S. Roy, M. Soon, S. Strom, D. Thibault, K.L. Vergin, F.A. Whitney, and C.S. Wong "Transformations of Biogenic Particles from the Pelagic to the Deep Ocean Realm," *Deep-Sea Research II* (in press).

M.A. Charette, S.B. Moran, and J.K.B. Bishop, "[234]Th as a Tracer of Particulate Organic Carbon Export in the Subarctic Northeast Pacific Ocean," *Deep-Sea Research II* (in press).

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Global Climate Change: Regional Effects and Potential Consequences of Adaptation and Mitigation Measures in California

Principal Investigator: Donald DePaolo

Project No.: 98009

Project Description

Bringing together scientists from LBNL and the newly formed Center for Atmospheric Sciences at UC Berkeley, this project is carrying out fundamental investigations that will help quantify the effects of global climate change.

In FY98, we conducted research on two areas of atmospheric moisture transport and atmospheric methyl bromide, applying a multidisciplinary approach. Results from these projects are described below. The funds were also used to help establish a capability in regional climate modeling and precipitation forecasting.

Accomplishments

Models for Global Atmospheric Moisture Transport and Implications for Isotopic Paleotemperature Records in Ice Cores

Much of our knowledge of the parameters and speed of global climate change is based on paleotemperature records retrieved from glacial ice in Antarctica and Greenland. These paleotemperature estimates are based on measurements of the isotopic composition of oxygen and hydrogen (normally expressed as $\delta^{18}O$ and δD) in ice. The glacial ice represents snow precipitated and accumulated over the past 200 to 300 thousand years. The conversion of water isotope ratios to mean annual temperature is uncertain. Current estimates are based on the modern observed relationship between $\delta^{18}O$ of snow and

mean annual temperature, but this may not apply during times when the climate is much different from today's. The objective of this research is (1) to develop a relatively simple model of meridional moisture transport and use it to evaluate the controls on $\delta^{18}O$ and δD of precipitation and (2) to reevaluate the isotopic data from polar ice cores in terms of paleotemperatures.

A model of meridional water vapor transport was developed and used to evaluate the factors that control the spatial and temporal variations of oxygen ($\delta^{18}O$) and hydrogen (δD) isotopic ratios in global precipitation. The model is based on meteorologic characteristics of the earth and extends Rayleigh-type models by including (1) effects of recharge to air masses by evaporation and (2) horizontal transport by both eddy-fluxes and advection. We find that globally, spatial variations in precipitation $\delta^{18}O$ and δD depend on the ratio of evaporation to the product of horizontal moisture flux and horizontal temperature gradient. At high latitudes, where this ratio is small and $\delta^{18}O$ and δD vary strongly with temperature, $\delta^{18}O$, δD, and deuterium excess depend on the ratio of advective transport to eddy transport. Transport by eddy-fluxes induces less fractionation than transport by advection, resulting in a smaller gradient of isotopic ratios with temperature. The temporal relationship between $\delta^{18}O$ (or δD) and temperature in Antarctica, which is necessary to estimate glacial period temperatures from $\delta^{18}O$ (or δD) measurements of ice, generally does not coincide with the modern spatial relationship and depends strongly on the proximity of the precipitation site to the ocean evaporation source. Sensitivity of $\delta^{18}O$ to temporal changes in local surface temperature is low at coastal sites and increases with distance inland. This model provides an explanation of the apparent discrepancy between borehole temperature inversion estimates of glacial temperatures and temperatures inferred from the modern spatial $\delta^{18}O$–surface temperature relationship. We concluded that (1) the temperatures at the poles of the earth were much colder (approximately 20° C instead of 10° C) during the last glacial period than had been previously estimated and (2) low latitude temperatures were lower by several degrees.

Isotopic Approach to Determining Industrial Contribution to Atmospheric Methyl Bromide

Methyl bromide (CH_3Br) is a trace gas that constitutes the primary source of stratospheric bromine. The role of bromine in stratospheric ozone loss has been well

documented, but the CH_3Br budget of the troposphere has major uncertainties. Because CH_3Br is produced by both industrial and nonindustrial processes, there are large uncertainties in estimating the industrial contribution. The fraction of tropospheric CH_3Br contributed by industrial production could be as low as 10% or as high as 50%.

We made measurements of the carbon isotopic composition ($\delta^{13}C$) of industrial CH_3Br. The results suggest (1) that the $\delta^{13}C$ values of industrial and nonindustrial CH_3Br sources are different by about 30‰ and (2) that, therefore, the $\delta^{13}C$ of atmospheric CH_3Br should allow accurate estimation of the industrial contribution. Samples of CH_3Br were obtained from the three largest manufacturers (Albemarle, Dead Sea Bromine, Great Lakes Chemical Co.) for isotopic analysis. These companies manufacture approximately 80% of the world's total amount of CH_3Br used as a fumigant. Aliquots of each sample tank were prepared by sealed tube combustion and analyzed on a dual inlet VG Prism mass spectrometer. They were also measured on a gas chromatography isotope ratio mass spectrometer (GC-IRMS) at LBNL, which allows separation of CH_3Br from other gas species, combustion, and carbon isotope analysis in a continuous flow mode and dramatically reduces sample size requirements (by a factor of $10^3 - 10^4$) compared to dual inlet mass spectrometry. Even with this increased sensitivity, measuring the $\delta^{13}C$ of CH_3Br from nonindustrial sources and the ambient atmosphere requires significant cryogenic preconcentration.

The measured $\delta^{13}C$ values of industrially produced CH_3Br are all low, but there is significant variability among manufacturers. The lowest value is about –68‰, and the highest is –48‰. The CH_3Br from the largest of the manufacturers (Ameribrom) has the highest $\delta^{13}C$ value. The industrial CH_3Br source is isotopically light, probably because thermogenic methane is used as a carbon source for methanol, which in turn is the feedstock for manufacturing CH_3Br. The average $\delta^{13}C$ of the industrial CH_3Br source, weighted by production values, is –56‰. The value expected for the natural sources of CH_3Br is about –20‰.

We also performed experiments to begin evaluation of the isotopic fractionations associated with bacterial degradation of CH_3Br. These experiments show significant fractionation, which must be accounted for in assessing the global mass balance.

Continued isotopic measurements of the primary CH_3Br sources and the atmospheric reservoir should greatly improve our understanding of the CH_3Br budget and the biogeochemical processes controlling atmospheric CH_3Br. This approach will also provide an independent tool for assessing the effectiveness of recent amendments to the Montreal Protocol that call for the complete phaseout of CH_3Br by 2005 in industrialized nations.

Drivers of Soil Carbon Storage in Terrestrial Ecosystems

Progress was made on (1) a mechanically based landscape scale model for soil carbon stocks in terrestrial ecosystems and (2) initiation of a soil carbon and land-use project (SCALUP) for the state of California.

The soil carbon model was developed to predict variations in near surface soil carbon stocks as functions of readily observable soil physical properties, climate, and vegetation community and productivity. The model predictions of soil carbon compared favorably ($r^2 = 0.67$) with measured data from an elevation gradient in montane meadows. Products of this work include (1) a talk describing the model and the model-measurement comparison that was presented at the Fall 1998 AGU meeting and (2) a manuscript that will be submitted to *Ecological Applications.*

Initial work on SCALUP was the assembly of a set of geographically explicit data bases of soil properties and historical and contemporary vegetation cover. Those maps were used to produce a map of soil carbon stocks that was used to identify several areas of interest for further study. Three of these areas include forested regions of Northern California, agricultural regions in the South Western San Joaquin Valley, and wetlands of the Sacramento-San Joaquin Delta. Present work now focuses on obtaining and synthesizing information from these areas. These efforts now involve collaborations with researchers at UC Berkeley and the US Geological Survey.

Regional Climate System Modeling and Analysis

From January through September 1998, N. Miller and J. Kim established a regional climate system modeling and analysis center at LBNL. The center completed 1997–1998 winter season hydroclimate studies of 48-hour quantitative precipitation and streamflow predictions and a new experimental seasonal forecast. Kim and Miller presented these results at the Third Campus-Laboratory-Collaboration Workshop at Los Alamos in May 1998. The 48-hour predictions are

used by the National Weather Service Sacramento Office as part of its analysis of California weather and for flood warnings. In collaboration with UC San Diego, UC Los Angeles, UC Davis, and the NOAA/National Centers for Environmental Predictions, the experimental seasonal prediction experiment represents an initial physically-based approach to forecasting three-month seasonal climate variabilities and extremes.

The initial LDRD support helped win two important grants: the NASA-supported California Water Resources Research and Applications Center at $1.5M and the LDRD-supported "Effects of 2xCO Climate Forcing on Western United States" for FY99. In addition, Miller and Kim now have several proposals to expand this research in review.

Related activities based on LDRD support include development of the DOE Accelerated Climate Prediction Initiative (ACPI) White Paper on Regional Climate Prediction and Assessment Centers.

This research involved the following personnel in addition to the principal investigator: Allen Goldstein (UCB and EETD), Sean McCauley (UCB and ESD), Mark Conrad (ESD), Melissa Hendricks (UCB and ESD), Marc Fischer (EETD), Norman Miller (ESD), and Jinwon Kim (ESD).

Publications

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M.B. Hendricks, D.J. DePaolo, and R.C. Cohen, "Space and Time Variation of $\delta^{18}O$ and δD in Precipitation: Can Paleotemperature Be Estimated from Ice Cores?" (to be submitted to *Science*).

S. McCauley, A. Goldstein, and D.J. DePaolo, "An Isotopic Approach to Determine the Industrial Fraction of the Total CH_3Br Source to the Atmosphere" (to be submitted to Proceedings of National Academy of Sciences).

M.L. Fischer, S.R. Saleska, J.A. Dunne, and J. Harte, "Soil Carbon in Montane Meadows Modulated by Climate and Vegetation Along an Elevation Gradient," AGU 1998 Fall Meeting.

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N.L. Miller, J. Kim, J. Farrara, K. Mo, and D. Cayan, "Short-Term and Seasonal Streamflow Predictions for a California Coastal Basin During the 1997–1998 Winter," American Metorological Society Meeting (January 1998).

Electromagnetic Methods for Fluid Emplacement and Monitoring in Subsurface

Principal Investigator: George Moridis

Project No.: 97008

Project Description

The objectives of this project are to investigate the potential of ferrofluids (stable suspensions of colloidal ferromagnetic particles in a carrier liquid) to (1) accurately and effectively guide reactants (for *in situ* treatment) or barrier liquids (low-viscosity permeation grouts) to contaminated target zones in the subsurface using electromagnetic forces and (2) trace the movement and position of liquids injected in the subsurface, using geophysical methods.

Ferrofluid Properties

Ferrofluids are stable colloidal suspensions of magnetic particles in various carrier liquids with very high saturation magnetizations (100–2,600 Gauss). The solid, magnetic, single-domain particles have an average diameter of 3–15 nm and are covered with a molecular layer of a dispersant. Thermal agitation (Brownian motion) keeps the particles suspended, while the dispersant coating prevents the particles from agglomeration. Ferrofluids are super-paramagnetic and move as a homogeneous single-phase fluid under the influence of a magnetic field. This attribute is responsible for the unique property of ferrofluids that they can be manipulated in virtually any fashion, defying gravitational or viscous forces in response to external magnetic fields.

Ferrofluids for Guiding Liquids in the Subsurface

Ferrofluids for guiding liquids (FGs) have low viscosities (<5 cp, allowing easy injection into the subsurface), small particle size (3.5–15 nm, minimizing potential filtration problems), and a very high saturation magnetization (100–2,600 Gauss). The ability of FGs to be guided precisely to specific areas in response to an external field has potentially important applications in the environmental restoration of the subsurface. We investigated the potential use of FGs to enhance the efficiency of *in situ* treatment and waste containment through (1) accurate guidance and delivery of reagent liquids to the desired subsurface contamination targets and/or (2) effective sweeping of the contaminated zone as FGs move from the application point to an attracting magnet/collection point. FGs can be manufactured with the appropriate carrier liquids, reactants (e.g., oxidants) for *in situ* treatment, and barrier liquids.

Ferrofluids for Tracing and Detection of Liquids

Because of their strong electromagnetic signature, ferrofluids for tracing liquids (FTs) are used commercially for magnetic pattern recognition in magnetic tapes, hard and floppy disks, and crystalline and amorphous alloys. The high saturation magnetization in the FGs provides a signature sufficiently strong for magnetic detection methods at low loading volumes (i.e., 1–5%). In FY97, we completed our investigation of the potential use of this property to (1) monitor liquid movement and position during injection and (2) detect and verify subsurface containment systems.

Accomplishments

Theoretical and Numerical Analysis

Analytical solutions were developed for an FG moving in an FG-saturated medium in response to a magnetic field with two different types of boundary conditions. Using a linear kinetic model, we developed analytical solutions to the problem of transport, filtration, and declogging of an FG through a porous medium. The analytical solutions of flow and transport were confirmed against experimental data.

From laboratory experiments, we determined that ferrofluids can display both miscible and immiscible behaviors with water, depending on the external magnetic field strength. Using the TOUGH2 general simulator of flow and transport through porous media, we developed ferrofluid simulation capabilities for both fully miscible and immiscible (two-phase) conceptualizations. The behavior and flow of miscible and immiscible ferrofluids in the presence of a magnetic field is described by the new TOUGH2 modules EOF7M and T2VOCM, respectively. Comparisons of the numerical solutions to laboratory studies show a good agreement between observations and predictions. Further development of these models is needed, however, to describe the reconcentration of dilute ferrofluids in the presence of an external magnetic field.

Laboratory Studies

We conducted the following experiments in FY98:

- An investigation of the force or magneto-pressure created in a ferrofluid by an external magnetic field.

- An evaluation of the magnitude and effect of ferrofluid filtration through porous media.

- A study of the effect of the magnetic field on the water miscibility and segregation of diluted ferrofluids.

- Design of magnetic fields for ferrofluid guidance and positioning in two- and three-dimensional systems, e.g., horizontal and vertical Hele-Shaw cells and sand trays and small-scale physical models of the subsurface tanks at the Hanford reservation. The magnetic field design experiments involved flow visualization, and several were used to validate the numerical models.

Our experiments showed that the magnitude of the magnetopressure and the distance over which it is effectively exerted increases with the strength and gradient of the magnetic field and the saturation magnetization of the fluid. The flow of ferrofluids through a limited number of soils showed no adverse effects on ferrofluid strength or stability through either filtration or reaction. Experiments investigating the magnetically-controlled miscibility of ferrofluids showed that, in the presence of an external magnetic field, the original ferrofluid can be recovered from a diluted ferrofluid and the miscibility of an otherwise fully water-miscible ferrofluid is inhibited.

The horizontal and vertical Hele-Shaw experiments confirmed earlier observations that, in the presence of an external magnetic field, the final distribution of a ferrofluid is easily predictable and controlled only by the magnetic field. The properties and heterogeneity of the porous medium have no effect on the final distribution, but they affect the flow pathway and the rate of ferrofluid accumulation against the magnet.
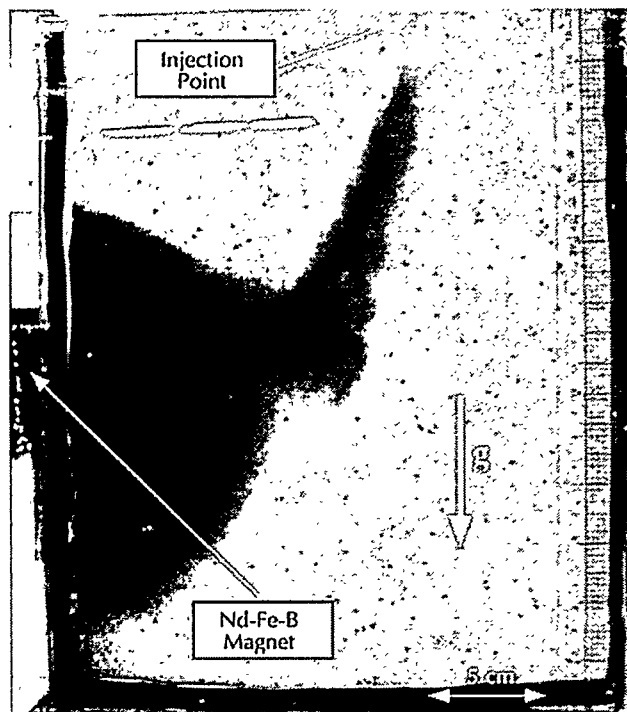
Figure 1. *Flow of EMG 805 ferrofluid through water-saturated sand toward a magnet in a vertical two-dimensional experiment. Ferrofluid is trapped by the magnetic field, defies gravity, and accumulates symmetrically against the wall without ever reaching the bottom.*

Vertical Hele-Shaw and sand-filled cells, designed to observe the combined effect of the magnetic and gravitational fields on the movement of ferrofluid, showed (1) that the ferrofluid formed a static arc-shaped pool around the magnet similar to that observed in the horizontal cells and (2) that, in the vicinity of the magnet, gravity is overcome by the strong magnetic field strength. See Figure 1.

Magnetic fields were designed to effect an accumulation of ferrofluid around, and encapsulation of, a three-dimensional, small-scale physical model of a buried tank at Hanford. This experiment exploited the enhancement of the magnetic field by the metallic material of the tank model and determined that the ferrofluid accumulation against the physical model could be made uniform and continuous. The implication of this observation is that ferrofluids with appropriate barrier carrier liquids can be accurately guided to and positioned in the subsurface and, on solidification of the barrier carrier liquid, can create barriers surrounding contaminated target zones. Similarly, ferrofluids with reactant-laden carrier liquids can be appropriately positioned using magnetic fields to intercept and treat *in situ* contaminated groundwater.

Publications

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Reactive Chemical Transport in Geologic Media

Principal Investigators: Karsten Pruess and George Brimhall

Project No.: 96031

Project Description

The purpose of this project is to develop a detailed three-dimensional simulation of the geologic evolution of an actual ore deposit through reactive porous media flow, subject to unique geologic constraints. The site chosen for the analysis is the El Salvador mine, located in the Atacama desert of northern Chile. El Salvador is operated by CODELCO, whose database of ore grades derived from 11,000 drill holes is available to the project.

The site-specific modeling effort will determine the interplay between paleoclimatic change, hydrogeologic conditions, erosion and uplift, and the mobilization and enrichment of massive amounts of copper-bearing minerals in response to spatially and temporally varying redox conditions. TOUGH2, LBNL's general-purpose, multiphase, multicomponent simulator, will model the evolution of hydrogeologic conditions over geologic time. The simulator is also being enhanced to describe the transport of chemical species subject to kinetic and equilibrium-controlled reactions, and is ported to advanced massively parallel computing platforms.

Results from the project are expected to aid in future exploration efforts for porphyry copper deposits and in the management of acid mine waters, leach dumps, mine tailings, waste disposal, and hydrothermal convection system. The reactive chemical transport capabilities will also be useful for assessing and remediating environmental contamination at DOE and industrial sites.

Accomplishments

Two reactive chemical transport simulators, TOUGH2-EQ3/6 and TOUGHREACT, have been developed using a sequential solution approach. The former was obtained by coupling the general geochemical speciation code EQ3/6 to the non-isothermal multiphase flow code TOUGH2, while the geochemical speciation part of TOUGHREACT was developed in this project. An efficient equilibrium-kinetics speciation algorithm was developed and used. On the one hand, TOUGH2-EQ3/6 has comprehensive geochemical capabilities for aqueous species and secondary mineral products. It keeps track of the full EQ3/6 chemical database for each gridblock at each time step, and its process simulation capability is extremely computationally intensive. On the other hand, TOUGHREACT is much more efficient (approximately 100 times faster than TOUGH2-EQ3/6 for the supergene enrichment problem). TOUGH2-EQ3/6 is used first for a few gridblocks over a short time period, whereas TOUGHREACT initially uses the speciation and secondary mineral products obtained from TOUGH2-EQ3/6.

First developed on a PC computer, TOUGHREACT was then moved and tested on VAX and UNIX systems. Later, the simulator was ported to the Cray T3E at the National Energy Research Scientific Computing Center (NERSC), and a parallelized version was developed—resulting in significant improvement of computing efficiency.

TOUGHREACT provides a comprehensive description of rock-fluid interactions during fully transient, multi-phase, nonisothermal flow and transport in hydrologically and geochemically heterogeneous media. A wide range of subsurface thermo-physical-chemical processes is considered. The model can accommodate any number of chemical species present in liquid, gas, and solid phases. A variety of equilibrium chemical reactions is considered, such as aqueous complexation, gas dissolution/exsolution, cation exchange, and surface complexation. Mineral dissolution/precipitation can proceed, subject to either local equilibrium or kinetic conditions. The model is verified for a wide range of subsurface physical and chemical processes. Water quality in the Aquia Aquifer (Maryland) has been used for validation; the simulation results agree well with the field concentration measurements.

Four applications have been carried out using TOUGHREACT. The first application is pyrite oxidation in unsaturated-saturated media. Pyrite oxidation causes acidification, movement of metals, alteration of primary minerals, and development of secondary minerals. We compare the results with the code TOUGH2-CHEM, another enhanced version of

TOUGH2 that includes reactive chemical transport (developed by S. White of Industrial Research Ltd., New Zealand). Although two different methods were used, the results agree reasonably well when gas transport processes are considered. The second application consists of predicting thermal, hydrological, and chemical processes induced by emplacement of a strong heat source in unsaturated fractured rocks to simulate a high-level nuclear waste repository. Preliminary modeling results indicate the importance of considering hydrochemical interactions between fracture and matrix for this type of system. The third application is the simulation of chemical evolution in an irrigated soil, to demonstrate flow and reactive transport under ambient conditions in unsaturated porous media.

The fourth application, which motivated the code development project, is supergene copper enrichment, which involves oxidative weathering of pyrite (FeS_2) and chalcopyrite ($CuFeS_2$), and associated acidification that causes mobilization of metals in the unsaturated zone. Enriched ore deposits subsequently form in the reducing conditions below the water table. Alterations of primary minerals and the development of secondary minerals predicted by our model are consistent with observations in supergene copper deposits in the Atacama Desert, Northern Chile.

We first consider the supergene copper enrichment in a one-dimensional unsaturated-saturated porous medium flow. Oxygen is supplied to a protore containing pyrite and chalcopyrite as a dissolved species in infiltrating rainwaters (70 mm/year) as well as by gaseous diffusion from the land surface boundary. A vertical column of 20 m thickness was modeled. (The top 10 m represent the unsaturated zone, while the bottom 10 m represent the water-saturated zone.) A steady-state water flow regime is assumed throughout. The column is initially filled entirely with a protore mineral assemblage (pyrite, chalcopyrite, magnetite, K-feldspar, albite, anorthite, annite, muscovite, anhydrite , quartz). Dissolution of the protore minerals is kinetically controlled. The precipitation of secondary minerals (covellite, chalcocite, bornite, goethite, hematite, kaolinite, alunite, and amorphous silica) is modeled as instantaneous during the simulation progress.

A dilute oxidizing water in equilibrium with an oxygen partial pressure of 0.2 bar is initially placed in the unsaturated gridblocks, while a reducing water with a partial oxygen pressure of 1.0×10^{-70} bar is assumed for the remaining (saturated) gridblocks.

The infiltration water composition is the same as the initial unsaturated water. A total of 52 aqueous species is considered. In the unsaturated zone, pyrite and chalcopyrite are oxidized and dissolved as follows (see Figure 1a):

$$FeS_2 \text{ (pyrite)} + H_2O + 3.5O_2(aq) \rightarrow 2SO_4^{2-} + Fe^{2+} + 2H^+$$

$$CuFeS_2 \text{ (chalcopyrite)} + 4O_2(aq) \rightarrow 2SO_4^{2-} + Fe^{2+} + Cu^{2+}$$
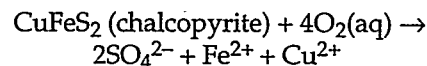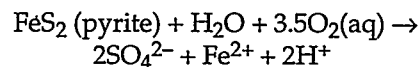
As aqueous-phase oxygen is depleted through reaction with pyrite and chalcopyrite, it is replenished by dissolution from the gas phase and by diffusive transport from the atmospheric boundary at the land surface. The pH decreases, and the total dissolved Cu and S concentrations increase due to pyrite and chalcopyrite oxidation. When the aqueous solution reaches the reducing saturated zone, the secondary copper-bearing minerals chalcocite and covellite are precipitated as follows (Figure 1b):

$$Cu^{2+} + HS^- \rightarrow CuS \text{ (chalcocite)} + H^+$$

$$2Cu^+ + HS^- \rightarrow Cu^2S \text{ (covellite)} + H^+$$
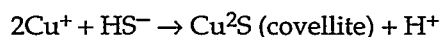
These minerals form the enrichment blanket immediately below the water table.

We then consider the supergene copper enrichment in a fractured rock using the "multiple interacting continua" (MINC) method. The MINC concept is based on the notion that changes in fluid pressures and chemical concentrations will propagate rapidly through the fracture system, while invading the tight matrix blocks slowly. Therefore, changes in matrix conditions will (locally) be controlled by the distance from the fractures and can then be modeled by means of one-dimensional strings of nested grid-blocks. An idealized fractured porous medium with a set of equidistant vertical fractures is used. Because of symmetry, only one column of matrix blocks, with a fracture spacing of 0.5 m and a depth of 20 m, must be modeled.

The same rainwater infiltration rate as for the previous porous medium problem is used; all infiltration occurs in the fractures. Water pressure is held constant at 2 bar at the bottom, and the water table is located at a depth of 10 m. The steady-state water saturation obtained by ignoring chemical reactions is used as an initial condition for the calculation of reactive chemical transport.

The other conditions are unchanged from the previous porous-medium simulation. The tight rock matrix is almost water saturated, and oxygen access is
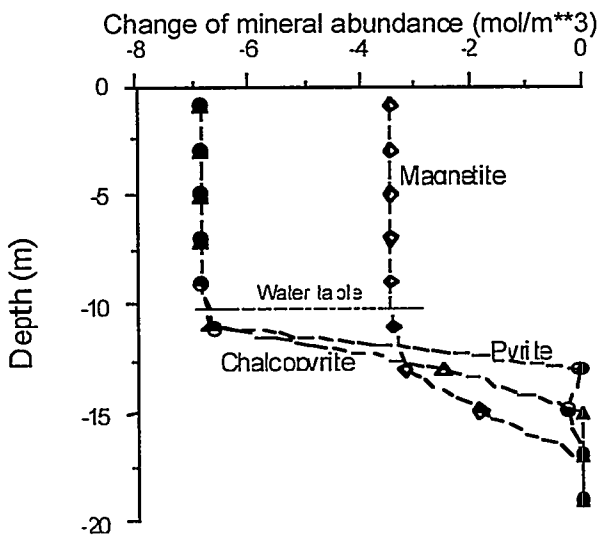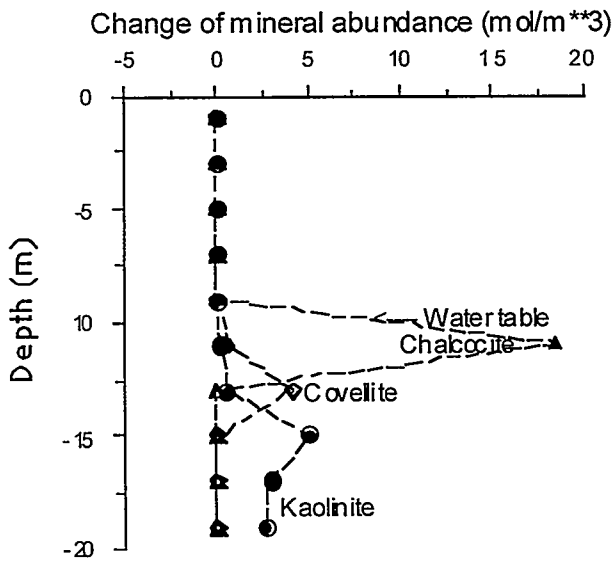
Figure 1. *Change of mineral abundance (in moles per cubic meter medium) after 90 years. Negative values indicate dissolution, positive indicate precipitation.*

Figure 2. *Change of chalcopyrite and chalcocite abundance after 90 years. Pyrite dissolution follows the same pattern as chalcopyrite.*

impeded. Pyrite and chalcopyrite oxidative dissolution takes place mostly in close proximity to the unsaturated fracture zone (see Figure 2a). Away from the fracture zones, dissolution rates decrease. Chalcocite precipitation (Figure 2b) occurs mainly in the matrix just above the water table and also in the deep fracture far below the water table. A small amount of covellite precipitates in the deep fracture.

The pattern of precipitation is different from the previous porous medium system. In the saturated zone, most water flow is passed through the fracture.

The flux is much higher than in the previous case, so much more aqueous oxygen is available in the fracture, and the oxidizing zone is extended deeply.

Publications

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Development of Mixed Waste Bioremediation: Biodegradation of Complexing Agent, Ketone, and Heavy Metal Mixtures

Principal Investigators: William Stringfellow and Jennie Hunter-Cevera

Project No.: 97010

Project Description

The presence of complexing agents and ketones in mixed wastes directly and indirectly influences the migration of toxic metals and radionuclides from land disposal sites at DOE facilities. The objective of this research is to gain fundamental information concerning the fate of mixed wastes in biologically active environments. In this research, we hypothesize that biodegradation of organic components in mixed wastes will influence the biogeochemistry and mobility of co-contaminant actinides and metals. Results from this project will be used to support larger, longer-term research projects examining the bioremediation of mixed wastes containing both heavy metals and actinides.

Our approach has been to apply classic methods of microbial ecology and physiology to elucidate fundamental information needed for modeling the biogeochemistry and environmental fate of mixed wastes. The focus of this year's research has been to examine the impact of metal-EDTA complexes on the biodegradation of solvents found in mixed wastes. We are interested in examining the impact of individual metal-chelates on microbial processes driving actinide biogeochemistry, so that we can identify the major variables of importance to modeling actinide migration in the subsurface.

Accomplishments

The first year of study focused on the isolation and characterization of microorganisms capable of degrading the ketone solvents. The second year of study examined how (1) biomass formed during ketone solvent degradation could adsorb actinides and (2) co-occurring contaminants found in mixed wastes at the Hanford facility could impact biomass formation. In particular, the impact of metals and metal-EDTA complexes on ketone biodegradation and biomass formation was evaluated.

Mixed wastes at the Hanford site contain high concentrations of nitrate. Nitrate was examined for its influence on ketone metabolism and bacteria growth under both oxygen-limited and anaerobic conditions. Under oxygen-limited conditions, nitrate stimulated the growth of the ketone-degrading mixed culture. Under strictly anaerobic conditions, nitrate did not serve as an electron acceptor for ketone degradation.

Metals and metal ethylene diamine tetraacetic acid (EDTA) complexes had a significant negative impact on ketone metabolism, depending on the metal in the complex. Copper-EDTA was the most toxic complex tested to date. Surprisingly, lead-EDTA did not inhibit ketone metabolism at the concentrations tested. The impact of metal complexes on biomass formation is being used to model how mixed wastes can influence biofilm formation and plutonium migration in the subsurface.

Publications

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Advanced Computing for Geophysical Inverse Problems

Principal Investigators: Donald Vasco, Lane Johnson, and Barbara Romanowicz

Project No.: 96033

Project Description

In the first half of this project, we are using several million seismic travel times and massively parallel computing to produce the first three-dimensional image of the structure of the entire earth (crust, mantle, outer core, and inner core). In addition, we simultaneously estimate the topography of the internal boundaries of the earth, e.g., the core-mantle boundary. In particular, we create an image of the outer core—the region in which the earth's magnetic field is generated. Recent three-dimensional numerical models of convection in the core have generated renewed interest in this region. Our results indicate intriguing coherent structure in the lowermost region of the outer core, which may be related to the convection process. This structure has never been imaged before, and the facilities at NERSC are allowing us to obtain a rigorous inversion of the seismic data.

In the second half of this project, we are using observations routinely gathered by petroleum engineers to infer the permeability and porosity distribution in a reservoir. Elucidating the three-dimensional porosity and permeability structure of oil and gas reservoirs is a primary problem for the petroleum industry. Unfortunately, little data exists that can be used to estimate porosity and permeability variations. One form of data recorded in almost all oil fields is the water to oil ratio of the fluid pumped from the wells. This ratio determines whether the well is economical and should be

maintained or shut down. The relationship between water-cut and the porosity and permeability structure of a reservoir is highly nonlinear, however, and no one has been able to analyze such information or relate it to the three-dimensional reservoir structure. Recently, we have developed an efficient algorithm for the inversion of such production data for reservoir structure.

Accomplishments

Using the T3E at NERSC, we have produced the first estimates of resolution and uncertainty associated with a three-dimensional model of the structure of the earth. A block Lanczos code has been developed and tested on the T3E and used to construct the estimates, which complement our new model of the structure of the entire earth. In addition, we have extended our work to assess a fine-scale model of earth structure. After dividing the earth into approximately 100,000 cells, we solve for the seismic velocity in each cell and are able to determine the reliability of inferred fine-scale velocity variations associated with subducting slabs.

Great progress has been made to determine reservoir structure based on data gathered from oil wells. Using data such as tracer concentrations and multiphase fractional flow data, we can infer reservoir porosity and permeability variations in three dimensions. A significant breakthrough allows us to map flow data into reservoir properties in a matter of hours rather than days or weeks of computation. In particular, we have developed an asymptotic technique similar to seismic and medical tomography, which is orders of magnitude faster than existing methods. We have extended this approach to the inversion of multiphase fractional flow data.

A completely new approach for solving nonlinear inverse problems has also been devised. Our methodology takes advantage of recent developments in computational algebra and commutative algebra. The underlying idea is that many nonlinear geophysical inverse problems reduce to systems of polynomial equations when written in discrete form. New algorithms based on Grobner basis calculations can provide answers to important questions concerning uniqueness and the existence of solutions to inverse problems.

Publications

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Tracer Tomography," *Water Resources Research* (in press, 1999).

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Engineering Division

Biosensor Development

Principal Investigators: Joseph Jaklevic and Mark Alper

Project No.: 98015

Project Description

An increasing need exists for the development of a variety of sensors to detect environmental contaminants, biohazards, and disease-causing agents (including bacteria, viruses and toxins, and biological and chemical-warfare agents). This project will utilize strong multidisciplinary support from LBNL Engineering, Materials Sciences, and Biology Divisions to address these needs.

Our approach will be to pursue research based initially on the following modalities of detection: electrochemiluminescence detection of target species, fiber-optic sensors using fluorescent labels, SQUID detection of altered magnetic effects on binding of target analytes. All of these techniques are based on areas of research at LBNL in which current expertise already exists, making it practical to implement them on a short time scale.

Accomplishments

Optical Methods

We have designed two biosensor systems: the first is based on electrochemiluminescence (ECL) detection, and the second is a fiber-optic based sensor. The ECL sensor is well characterized, and the reaction chemistry is established. Our adaptation of ECL as a biosensor is relatively unique and built on considerable expertise gained during the earlier development stage. The system has been tested with a lysozyme antibody-antigen pair to demonstrate applicability for biosensor development. The strengths of this system are parts-per-billion sensitivities, adaptability to a wide range of antibody-antigen pairs, compact size, "hands off" operation, high multichannel throughput, and minimized risk of exposure to users through complete containment and post-detection denaturation of the analytes (which can include biotoxins and viruses).

Fiber-optic sensors are widely utilized in the field of biosensors because of their versatility of design and use. Our fiber-optic system has undergone initial testing, and considerable progress has been made in optimizing the geometries of the sensing end of the fibers. Fiber-optic sensors boast many of the same advantages as ECL, but also provide for remote sensing, custom design of the fibers for varying environments, miniature size, ease of production, low cost, and adaptability to any detection scheme that results in light emission near the fiber surface. Our detector is intended to become a platform for an increasing array of bio-detection schemes and development/discovery of antibody-antigen-related interactions to further the scope of detectable bio-agents.

The ECL system is currently undergoing a brief development stage intended to further optimize the performance and detection sensitivity of the instrument. The ECL biosensor will then be ready for proofing with bio-agents of "real world" interest. In this direction, the instrument will be transported to R. Stevens' laboratory on the UC Berkeley campus, where several controlled bio-agents (such as botulin) will be used with the system.

The fiber-optic sensor is starting to be routinely used with collaborators in Stevens' group. The optical fiber-etching robot (which allows for uniform etching of fibers to specific geometries) is allowing for fine-tuning of the instruments' sensing fibers. Continuing with this project, we will explore and optimize the different fiber geometries we have generated and further develop test systems to demonstrate the sensors' utility. After the system has been proofed with several benign bio-agents, it will follow the ECL system to UC Berkeley and be applied to various bio-agents available only on that campus.

Magnetic Methods

We have proposed the development of a biosensor combining the peculiar magnetic properties of small ferric oxide beads, the existence of binding sites for magnetic particles on analytes of interest, and the exquisite sensitivity of Superconducting Quantum Interference Devices (SQUIDs). Calculations suggest

that these devices will detect extremely small quantities of target.

A SQUID "microscope" can detect extremely small magnetic fields. Theoretical work performed as part of this project has predicted that a magnetic field can be detected in immobilized particles that have been briefly exposed to a magnetic field. In particles of an appropriate size, however, this field decays too rapidly for detection. This project then focused on capitalizing on this phenomenon by using the SQUID microscope to signal the presence of a bioactive agent such as a bacterium, virus, or toxin. Progress to date has shown that appropriately prepared magnetic particles can escape detection by the SQUID microscope as constructed by the group. The microscope does, however, detect a signal from immobilized particles, and that signal appears to scale with the amount of material being examined. In preliminary work, attachment of the particles to glass beads did allow detection of the signal, as did their attachment to individual bacterial cells.

Further controls are being imposed to demonstrate that the detection is specific for the target and is sufficiently sensitive for practical application.

Scanning Focused-Ion Beam Technology for High-Throughput, Magnetic Head Fabrication

Principal Investigator: Ka-Ngo Leung

Project No.: 98016

Project Description

Focused ion-beam (FIB) technology is used in pole-tip trimming applications as part of the fabrication process for magnetic heads. Conventional FIB systems use gallium ions, which need to be removed from the airbearing surface for reliability reasons. In addition, the ion-beam current is only in the nanoampere range, which means low throughput. With significant advancements in ion-beam technology at LBNL, direct-surface milling and patterning (by scanning FIB) of gaseous ions such as krypton and xenon can be made practical for high-volume production.

In the proposed fast-scanning FIB system, we will use a multicusp ion source, rather than a liquid-metal ion

source, to achieve the required current densities. One of the advantages of the multicusp ion source is that it can produce nearly any type of ion beam. As a result of the magnets that produce cusp fields, the source generates large volumes of uniform quiescent plasmas. The axial ion energy spread of this source is below 1 eV, and the output current density is high (>250 mA/cm^2) for steady-state operation. The accelerator column will be made of several electrodes to extract and focus the beam. The column is designed using an ion optics code IGUN.

Accomplishments

A 5-cm-diameter multicusp ion source has been fabricated and assembled. This ion source is capable of producing all types of gaseous ions and even metallic ions. The source was mounted on the new test facility constructed for this FIB application. A FIB column for a 50-keV ion beam has been fabricated. The electrodes used for the column were 0.5 mm thick, and the minimum hole diameter size was 100 mm, so that the entire column is less than 3 cm long. Tested for high voltage holdup and beam transmission, the accelerator demonstrated that its column can hold up to 45 keV and that it can obtain beam currents of a few mA—at least an order of magnitude greater than conventional systems.

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Environmental Energy Technologies Division

Direct-Ethanol Fuel Cells

Principal Investigator: Elton Cairns

Project No.: 97011

Project Description

The goal of this project is to improve the performance of direct-ethanol fuel cells to meet or approach the performance requirements of electric vehicles. This exploratory effort will focus on the testing and analysis of direct-ethanol fuel cells utilizing advanced Pt-containing electrocatalysts, polymer electrolytes, and alkaline Cs_2CO_3-based electrolytes for the direct electrochemical oxidation of ethanol.

The first phase of the project is the construction of the equipment necessary for the operation of laboratory cells at elevated temperatures up to 200° C and elevated pressures up to several atmospheres. This equipment must include provision for accurate flow control, humidification of fuel and air streams, and the analysis of products. In addition, facilities and equipment for the preparation of electrodes and membrane-electrode assemblies are necessary.

Accomplishments

This project requires the design and construction of (1) improved cell components and (2) a cell chamber for operation at elevated temperatures (up to 200° C) and pressures (up to several atmospheres). These permit a thorough investigation of reaction rates over a significant range of operating conditions. The cell components have been fabricated and tested for leak-tightness. The cell chamber has been designed and constructed. Electrode fabrication techniques have been established for the proton exchange membrane (PEM) cell, which outperform their commercially available counterparts. A comparison of the performance of the commercial type of electrode (impregnated) with our electrode (air brushed) is shown in Figure 1. Modeling efforts to optimize cell operating conditions and construction were done. Initial studies with alcohol fuels have yielded the expected results. Further testing under more rigorous operating conditions has also been done. Preliminary selection of new electrocatalysts based on Pt-containing alloys supported on carbon has been undertaken along with methods of preparing them in both supported and unsupported forms.
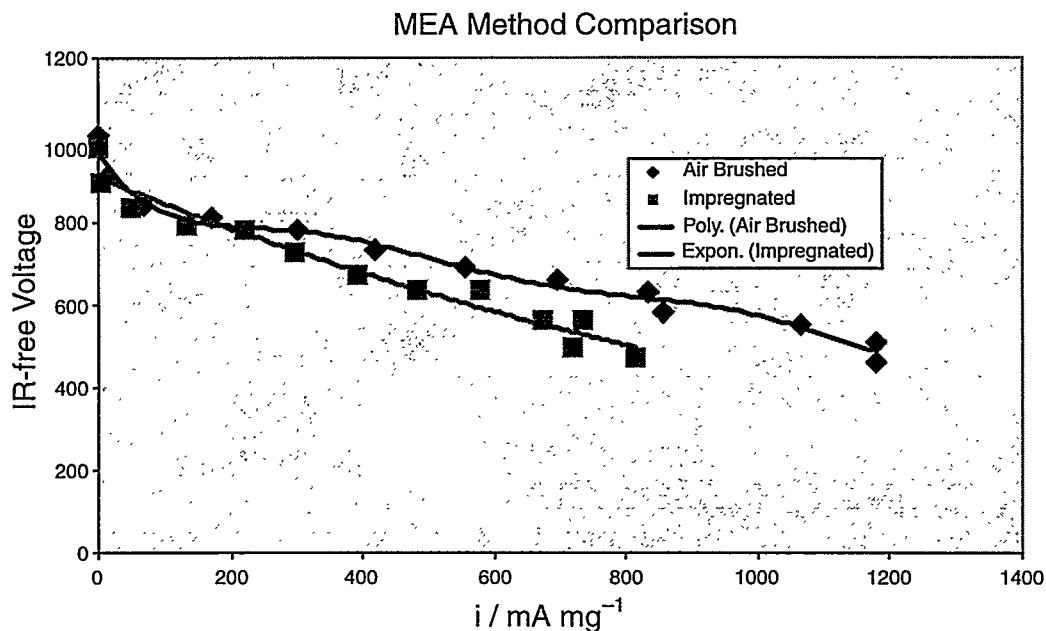
Figure 1. Comparison of Hydrogen/Oxygen Performance on Commercial (Impregnated) and LBNL Air-Brushed Electrodes

Fundamental Research on Lean Premixed Combustion for Gas Turbine Technology

Principal Investigator: Robert Cheng

Project No.: 98010

Project Description

Lean premixed (LP) combustion is an emerging environmental energy technology that is being developed to reduce the emissions of undesirable combustion byproducts from gas turbines. LP combustion emits only one-tenth to one-twentieth the amount of oxides of nitrogen (NO_x) as conventional methods, but development of LP gas turbine combustors presents many engineering and technical challenges. Under gas turbine conditions of high pressures and elevated inlet temperatures, LP flames are prone to instabilities and blow-off. The scientific objective of this project is to improve our understanding of LP combustion in gas turbines by elucidating the fluid mechanic processes pertaining to stability, flame propagation, and emissions. Such basic scientific knowledge is essential to guide the design of gas turbine combustors as well as the development of software tools for engineering designs.

The LDRD fund supports the design and construction of a laboratory scale experimental facility that allows the use of advance laser diagnostic to probe turbulent LP flames at elevated inlet temperatures and high pressures. This equipment is necessary for achieving our scientific objective.

Accomplishments

The first phase of this project is the design and construction of a facility that accommodates LP flame experiments at pressures up to 5 atmospheres but without a preheater for increasing the inlet temperature. This system will permit investigation of LP flame behavior up to the idling and mid-load conditions of a small gas turbine combustor. The facility is designed to operate up to 15 atmospheres with a preheat inlet temperature of 200° C. The second phase of the project is to upgrade to these higher operating temperatures and pressures.

The centerpiece of the equipment is a stainless steel combustion chamber that mounts on top of a premixed burner. The combustion chamber is fitted with four 25.4 mm thick, 101.6 mm round sapphire windows to allow direct optical access to the flame. The burner has a 25.4 mm round exit port and can be adapted to generate different flame configurations. This facility includes computer control provisions to set the fuel and air streams accurately, monitor chamber pressure and surface temperatures, and analyze combustion byproducts. In addition, installation and equipment for delivering high-pressure air, de-pressurizing and cooling the exhaust stream, igniting the flame, and safeguarding users from accidental release of energy from the high-pressure system are necessary.

The combustion chamber has been tested, modified, and rated to pressures up to 30 atmospheres. The burner has been designed and constructed. To place this apparatus into existing optical paths of various laser diagnostics, the overall layout of the Combustion Laboratory has been rearranged, and the station is close to completion. The chamber/burner assembly with pilot flame ignitor is mounted on a raised platform on top of an optical table. All flow controls and electronic components have been installed. The assembly for the exhaust stream, which includes a heat exchanger and pressure release valve, is the only piece remaining to be fabricated. Testing of the flow controllers at room temperature and pressure is underway. Software for controlling the experiments and gathering performance and exhaust gas data has been written and is being tested. Start-up, shut-down, and emergency shut-off procedures are being developed.

Following completion of atmospheric testing of the chamber, flame experiments will commence at both atmospheric and high pressures. Because these high-pressure tests are potentially hazardous, we plan to begin with the weakest flames (at low flow rates), using the simplest burner configuration. Typical conditions will have flow velocities between 1 to 3 m/s. These tests will help us fine-tune the flow control protocol, rehearse the emergency shut-off procedure, and evaluate the integrity of the safety interlocks.

Air Pollution and Mortality: Significance of the Chemical Composition of Particulate Matter

Principal Investigator: Joan Daisey

Project No.: 98011

Project Description

Many recent epidemiology studies indicate that daily rates of mortality and morbidity increase as airborne particulate-matter (PM) concentrations increase and that these effects occur at concentrations below the PM standard. The studies have generally utilized simple metrics of particulate pollution, e.g., total suspended particulate matter, PM-10 (particles $\leq$ 10 μm, mass median aerodynamic diameter). PM is a complex mixture of particles originating from a number of sources, each of which typically emits particles with a distinctive chemical composition, particle size distribution, and biological potency. Scientists agree that identification of specific PM components associated with health effects is one of the highest-priority research needs. The objectives of this project are to evaluate (1) the role of chemical composition in relationships between mortality and PM, and (2) the utility of a new methodology for developing PM source-emissions metrics that can be directly related to health effects. The project takes advantage of a unique data set of PM measurements, which includes extensive chemical speciation and daily mortality data from three New Jersey cities (Newark, Elizabeth, and Camden).

Accomplishments

In the first year of this project, we have found the first epidemiological evidence of relationships between the chemical composition of airborne PM from different sources of PM and daily mortality rates, using the new methodology. The new methodology separates the components of PM by emission sources and their chemical composition. Several metrics, representing the fractions of PM from residual oil burning, industrial sources, and motor vehicle emissions, were statistically significant predictors of total mortality. The results for total mortality (excluding accidental deaths) are summarized in Table 1.

In two of the cities in which residual oil was used for industrial boilers and electrical generation, there were statistically significant relationships between total mortality and the PM source-emissions metrics related to residual oil burning. The subset of cardiovascular deaths was also significantly related to oil-burning PM emissions. PM from zinc smelters in Newark was also related to total mortality as well as to cardiovascular mortality in this city. The motor-vehicle-emissions metric was a significant predictor of cardiovascular death only in Camden. For Elizabeth, no statistically significant relationships were found between total mortality and any of the source-emissions metrics. The relative risks for the PM source-emissions metrics are somewhat higher than those reported for PM and sulfate (~1.05), indicating that the method effectively resolves the fractions of PM mass most biologically relevant to daily mortality.

Table 1. Preliminary results: Source-related PM metrics related to total mortality rates in three New Jersey cities, 1981–1983.

City	Relative Risk[a]	Residual Oil-Burning	Industrial Sources[b]	Sulfate PM	Motor Vehicles
Newark	1.10 ± 0.03	+	+	+	NS
Elizabeth	NS	NS	NS	NS	NS
Camden	1.14 ± 0.04	+	NS	NS	+

+ Indicates that the source-emissions vector was a statistically significant predictor of cardiovascular mortality at the p $\leq$ 0.10 level; NS = not statistically significant; model controls for weather/seasonal effect.
[a]Relative risk is the ratio of the risks for exposed and hypothetical unexposed subjects.
[b]In Newark, the industrial sources that have high concentrations of Zn in the emitted PM, are zinc smelters.

The analyses also showed statistically significant ($p \leq 0.05$) relationships between total mortality and three simpler metrics of PM—inhalable particulate mass, fine particulate mass, or sulfate—in Newark and Camden, as shown in Table 2. This result is consistent with the results reported by other investigators for other cities.

In the next phase of this project, we will confirm and extend our analyses of relationships between the new PM source-emissions metrics for airborne PM and daily mortality (total and cardiovascular plus respiratory). We will conduct "lag time" analyses to take time delays between exposure and mortality into account and prepare a paper. We will also continue efforts to understand why none of the PM metrics is significantly related to mortality in Elizabeth.

Table 2. Preliminary results: Simpler PM metrics related to total mortality rates in three New Jersey cities, 1981–1983.

City	IPM	FPM	Sulfate
Newark	+	+	+
Elizabeth	NS	NS	NS
Camden	+	+	NS

+ Indicates that the source-emissions vector was a statistically significant predictor of cardiovascular mortality at the $p \leq 0.10$ level; NS = not statistically significant; model controls for weather/seasonal effect.

UV Disinfection: Field Test of a Small-Scale System

Principal Investigator: Ashok Gadgil

Project No.: 98036

Project Description

LBNL has developed a low-cost, robust, and energy-efficient ultraviolet (UV) technology (UV Waterworks) to disinfect drinking water in developing countries. This technology has passed careful tests in ten laboratories in five countries. Long-term field tests in real-world settings must be undertaken, however, to identify (and correct) any unforeseen shortcomings in this technology, its long-term performance, and its ability to disinfect the full annual range of challenge-water parameters. The goal of this project is to undertake a 12-month field test at one site in South Africa to determine the functioning of the unit under field conditions and its performance in disinfecting the annual range of challenge water.

Accomplishments

The first task of this project is to identify a field site for UV Waterworks to be tested for one year. This site must have local technical support for operation and maintenance, as well as labor (effort) and transport arrangements to collect water samples periodically throughout the year, and suitable laboratory facilities to test the samples for bacterial quality and report the results to us. We have tentatively identified a site in the Umzinyathi Water District of the KwaZulu-Natal state of South Africa.

This site, located outside the town of Dundee, is a primary health-care clinic built by the local community with its own labor. It has a small photovoltaic electrical pump system (and no grid-connected power). The photovoltaic system, donated by a North European community, is currently dedicated to pumping groundwater for the health-care clinic. Because it is a showcase facility supported by the Regional Council, the site is staffed full time. It has post-office boxes for the local community and a stand-pipe for water collection. Both the postal and water services are used by a few hundred people.

The water sample from this site shows good UV transmittance (equivalent to US tap water, $0.1/cm$ base e), giving us confidence that the water is suitable for UV disinfection. We also tested the water for biological contamination and found evidence of coliform contamination, possibly a result of a deep-drop toilet (the only one on the premises) established within 10 meters of the borehole that supplies groundwater to the clinic.

Organization of local and institutional support for collection and transport of water samples from the site (to be initiated after the field tests begin) is a vital part of this project, as is a laboratory where the samples can be analyzed and the results reported to us.

Mini-HID Lighting: Semiconductor Processing Technology for Energy Efficient Lighting

Principal Investigators: Steven Johnson and Michael Vella

Project No.: 98012

Project Description

This project will demonstrate and characterize new energy-efficient, miniature high-intensity discharge (mini-HID) light sources. When commercialized, mini-HIDs will offer a more energy-efficient alternative to incandescent lamps. Large, high-power, high-intensity discharge lamps have been commercially available for years in wattages ranging from 125 to 1000. Because of perceived cost barriers, low-power lamps suitable for residential and general use have not been developed. Compared with common incandescent sources, mini-HIDs will have equivalent luminous output, fit within the same glass envelope, and be four times more energy efficient. They will also be significantly smaller and less expensive than comparable compact fluorescent sources.

Small batches of mini-HIDs have been handmade to establish electrical characteristics and optimize design. The first batches were made in the LBNL glass shop, which lacks control of the process atmosphere. Several batches were then made under contract by a small commercial shop (Galaxy Glass), with better process control. Prototype lamps were characterized electrically. Due to oxygen contamination of the electrodes, the quartz envelop of the LBNL lamps darkened, so that emission characterization was pointless. The Galaxy lamps are much cleaner, and light emission will also be characterized.

To demonstrate an effective path to mass-market usage, prototypes will be made using wafer-based manufacturing adapted from a subset of semiconductor process tools. Wafer-based processing will be attempted later this year, using the wafer-planarization and wafer-bonding tools coming online in the UC Berkeley Electrical Engineering and Computing Sciences microfabrication laboratory. Quartz wafers (four inches in diameter) will be used initially. Advanced semiconductor grinding and

polishing techniques (chemical mechanical planarization) should produce the 100≈ flatness required for bonding.

Accomplishments

Basic parameters, such as arc length and electrode diameter, were varied to study device performance. The lamps were operated at low frequencies (60 Hz to 100 kHz). At first glance, the LBNL lamps appeared to have the negative volt-amp (V-I) characteristics expected for a plasma (i.e., voltage falls as current and power increase). V-I characteristics for the LBNL lamps are illustrated in Figure 1. The emission efficiency of the LBNL lamps could not be studied, because fabrication in a contaminated atmosphere led to oxidation of the electrodes and discoloration of the quartz.

The lamps fabricated by Galaxy were similar in size to those fabricated at LBNL, but displayed a surprising V-I characteristic; with a steep positive slope, as illustrated in Figure 2. The short arc lamps (2 mm)

LBL lamps
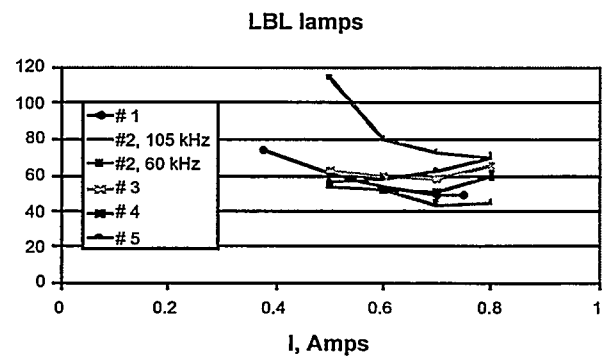
Figure 1. Volt-amp characteristics of LBNL fabricated mini-HID lamps.
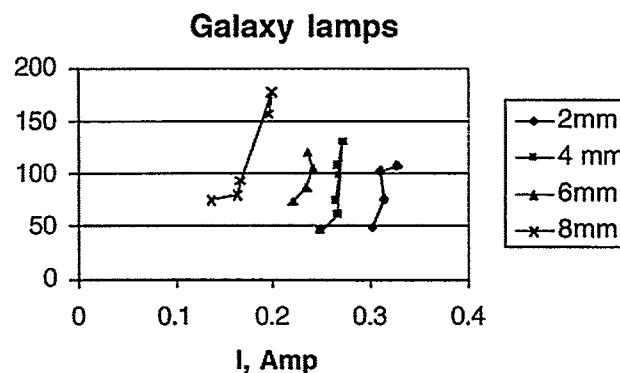
Galaxy lamps

Figure 2. Galaxy lamps display a positive volt-amp characteristics slope.

operated as low as 50 V, which should give long electrode life without contaminating the quartz envelope with sputtered tungsten. The extremely positive V-I slope is surprising and troublesome, however, because the only way to increase power is to increase voltage. In retrospect, some of the LBNL lamps also had a flat to slightly positive V-I. At the moment, our top priority is to learn how to produce a more desirable V-I characteristic.

Simulation and Experimental Investigation of Growth and Spatial Organization in Biodegradative, Mutualistic Multispecies Biofilm

Principal Investigator: Jay Keasling

Project No.: 98013

Project Description

The objective of our project was to understand interactions between multiple species in a biofilm and to use the mutualistic relationships in a biofilm culture to degrade or detoxify environmental contaminants. The project combined computer modeling and laboratory experimentation to achieve the stated goals. The specific aims were as follows:

(1) To develop a three-dimensional cellular automata simulation of a mixed-population biofilm by:

- Examining mutualistic interactions in a multi-species biofilm;

- Examining the effects of the mutualistic interactions on bioremediation; and

- Addressing physical issues within the biofilm.

(2) To develop a mutualistic biofilm culture that would detoxify/degrade recalcitrant environmental contaminants by:

- Validating predictions of the simulations;

- Obtaining key parameters for the simulation;

- Examining pattern formation of two microorganisms in a dual-species population;

- Examining the effect of environmental conditions on pattern formation; and

- Examining the utility of multispecies populations in degradation or detoxification of mixed wastes.

Computer modeling for this project was carried out in the Department of Chemical Engineering at UC Berkeley. Biofilm cultures were grown and maintained in the J. Keasling laboratory there. Analysis of the biofilm cultures was performed at the Advanced Light Source (ALS) at LBNL, in cooperation with the Center for X-Ray Optics, and in the experimental facilities of the Center for Environmental Biotechnology at LBNL.

Accomplishments

Computer Modeling of Heterogeneous Biofilm Growth and Development

A generalized stochastic simulation of biofilm growth and development was developed to describe the spatial and functional heterogeneity of multiple interacting species in a biofilm. The simulation represents the growth of microbial unit cells in a three-dimensional domain modeled after a repeating section of a constant depth film fermenter. Cell growth in the biofilm was assumed to be limited by a single substrate, the transport of which, like all other solutes in the simulation, was represented by Brownian diffusion. Other solutes accounted for in the simulation were cell growth inhibitors and secondary metabolites secreted by the cells. On division, one daughter cell replaced the mother cell and the other daughter cell displaced adjacent cells in the direction of least resistance. In addition to growth and division, the simulation also accounted for cell death. Any number of different microbial species and solute types, as well as interactions among them, can be accommodated in the biofilm growth simulation.

The simulation was implemented to study the results of various levels of transport limitation on a single species growing biofilm. In a system with rapid solute diffusion, cells throughout the biofilm grew at their maximum rate, and no solute gradient was formed over the biofilm thickness. In increasingly transport-limited systems, the rapidly growing fraction of the biofilm population decreased and was found exclusively at the biofilm-liquid interface. Trans-biofilm growth substrate gradients also deepened with increasing transport limitation.

Autoinhibitory biofilm growth was simulated for various rates of microbially-produced inhibitor transport. Inhibitor transport rates affected both the biofilm population dynamics and the resulting biofilm structures. The formation of networks of cell-sized void spaces in slow-growing regions of the biofilm suggested a mechanism for the

microscopically-observed evolution of channels in flow cell biofilms.

The simulation was also used to investigate the effects of various trophic interactions and interdependencies on multispecies biofilm population dynamics and structural organization. Binary biofilms exhibiting amensal, commensal, and mutualistic feeding interactions were examined. The stable coexistence of species in a multispecies biofilm was found to depend on the species' ability to maintain equal growth rates in the layer of the biofilm closest to the solid substratum. The substratum layer was also found to play a role in the extended survival of doomed microbial species in biofilms, compared with similar species in suspended culture. Cell death in the biofilms was necessary to allow the multispecies populations to approach their ultimate stable species compositions. Cell death also played an important role in the development of various biofilm structures. The structures observed in the binary biofilm simulations included vertical single-species clusters, uniformly interspersed mixtures of the two species, and horizontally-segregated layers of the species. Structures arose in response to interdependencies between biofilm species, and these interdependencies were found to rely on the development of solute gradients across the biofilm thickness. A decrease in solute gradients due to improved solute transport decoupled the biofilm species from one another and subsequently affected multispecies population dynamics and structural organization.

Investigation of Biofilm Structure and Development Through Laboratory Studies

In collaboration with W. Meyer-Ilse at the Center for X-Ray Optics, we examined the development of several biofilm cultures using soft x-ray microscopy. This work allowed us to directly observe the interlocking structure of intact, hydrated biofilms at high magnification. Work was carried out with several individual species and consortia, including *Pseudomonas putida* DMP-1, a phenol degrader, and *Xanthobacter autotrophicus* GJ10, a dichloroethane utilizer. We also developed a parallel plate flow cell that allows us to examine the formation of mutualistic biofilm populations. Analysis of fluorescently-labeled bacteria growing in the flow cell apparatus provided detailed information on the distribution of species within the biofilm culture. Biofilms of fluorescently-labeled bacteria were analyzed using a confocal scanning laser microscope in the experimental

facilities of the Center for Environmental Biotechnology.

Publications

N. Eliashberg and J.D. Keasling. "A Generalized Stochastic Simulation of Heterogeneous Biofilm Growth and Development, " *J. Theor. Biol.* (submitted 1998).

N. Eliashberg and J.D. Keasling. "Population Dynamics and Species Spatial Organization in Simulated Multispecies Biofilms, " *J. Theor. Biol.* (submitted 1998).

E.S. Gilbert, A. Khlebnikov, W. Meyer-Ilse, and J.D. Keasling. "Use of Soft X-Ray Microscopy for Analysis of Early-Stage Biofilm Formation," *Water Science and Technology* (in press 1998).

Electrocatalysis of Biological Processes for Remediation of Contaminated Soils

Principal Investigators: John Kerr, Fazle Rabbi, and William Stringfellow

Project No.: 98014

Project Description

The aim of this project is to develop understanding of the effects of electrokinetic soil remediation on intrinsic microbial activity for accelerated *in situ* biodegradation of organics and accelerated metals removal by biosorbent organisms. Electrokinetic soil treatment is a potentially powerful tool for enhancing bioremediation (see Figure 1). Because it is equally important to avoid misapplication of this treatment, the effects on indigenous biological activity must be thoroughly understood. This project will provide such knowledge by application of advanced chemical and biological methods to monitor changes. Contaminants to be studied will be chosen to provide experience with common environmental problems so that this knowledge may be rapidly applied to the field.
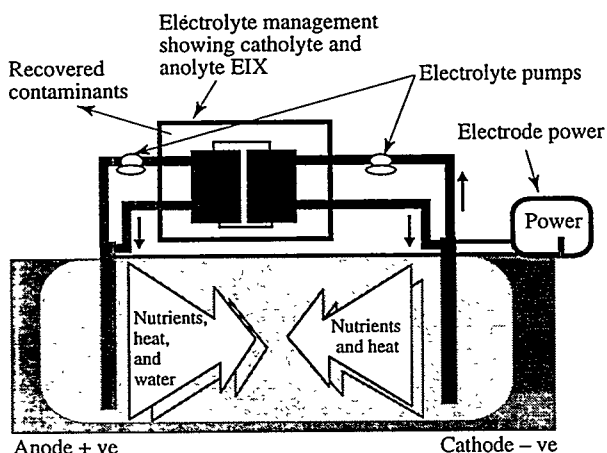
Figure 1. Schematic of "pool" process (US Patent 5,433,829) for use with bioremediation in soil.

Accomplishments

Two complete electrokinetic cell systems have been built and tested with uncontaminated soil samples. Figure 2 shows a schematic of the laboratory system, which shows half of a soil cell for simplicity. Not shown are temperature, pH, and redox potential sensors embedded in the soil. The resistive electrolytes and high voltages provide a considerable challenge for accurate pH sensing of the soil. Other factors such as pump rate in the electrolyte conditioning system have been varied to determine the important parameters to be closely controlled during experiments. The long duration of any particular experiment mandates that the conditions be well controlled.

In addition to engineering activities related to cell design and operation, analytical capabilities have been under development. Standard analyses for total petroleum hydrocarbon content and polyaromatic hydrocarbons (PAH) have been applied to follow the biological activity. Microbiological methods such as cell counting have been applied to samples taken from the electrode and sensor wells during the experiments, and chemical analyses of the ion concentrations have also been carried out. The use of capillary electrophoresis (CE) as an analytical method is also under study both for inorganic ion analysis and for organic analysis. CE has recently been shown to be a powerful tool for analysis of proteins, polynucleotides (DNA and RNA), and even whole enzymes. These measurements will provide useful data on the indigenous biological activity in the soil as the electrokinetic experiments proceed.
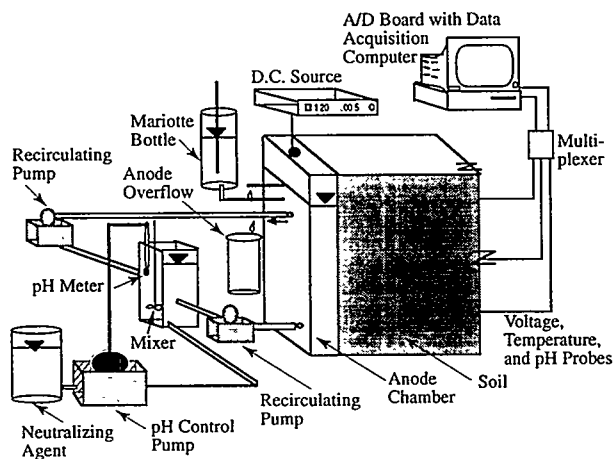
At this point the systems to produce useful results are all in place, and experiments with actual contaminated soil samples have begun. It is clear from the initial results that enhanced biological activity results from the heating effect of the current. After only one month of operation, the levels of organic contaminants have decreased. Further experiments are underway on actual contaminated soil from a local site where the use of electrokinetic remediation is under consideration as the clean-up method of choice.

Publications

J.B. Kerr, F. Rabbi, W.T. Stringfellow, R. Clarke, and R. Lageman, "Electrokinetic Effects on Bioremediation of Metal Ion and Organic Pollutants in Soil" (presented at ACS Boston National Meeting, August 1998).

J.B. Kerr, F. Rabbi, W.T. Stringfellow, and R. Clarke, "Electrokinetic Acceleration of Bioremediation of Metal Ion and Organic Pollutants in Soil" (submitted for presentation at ACS Anaheim National Meeting, March 1999).

J.B. Kerr, F. Rabbi, and W.T. Stringfellow, "Electrokinetic Acceleration of Bioremediation of PAH and Petroleum Hydrocarbon Contamination in Clay Soil" (in preparation).

J.B. Kerr, F. Rabbi, G. Klunder, and W.T. Stringfellow, "Application of Capillary Electrophoresis to Monitor Metal Ion Content and Biological Activity in Contaminated Soils Under Accelerated Bioremediation" (in preparation).

Figure 2. Laboratory set-up for electrokinetic experiments (only anode half of cell is shown).

Energy Efficiency and Demand in Industry: A Global Assessment

Principal Investigators: Mark Levine, Lee Schipper, Jayant Sathaye, Lynn Price, Nathan Martin, and Jonathan Sinton

Project No.: 97012

Project Description

The purpose of this project was to develop tools and data to significantly improve the analysis of how energy efficiency reduces greenhouse-gas emissions and contributes to national and regional economic-development objectives. By assessing energy use in the industrial sector of national, regional, and global energy systems, this project has led to new activity at LBNL involving energy efficiency in industry.

Our approach focused on analyzing the drivers of energy demand in major energy-using industrial subsectors, with an initial focus on iron and steel, cement, and pulp and paper production. This was accomplished by the establishment of, and our collaboration with, an international set of expert working groups to provide data, perform analysis, build analytical tools, and develop scenarios. The major activities involved a continuation of collecting higher quality disaggregated subsectoral data, analyzing technologies that can influence industrial energy use at the subsectoral level for various countries, building a network of collaborators so that the detailed data gathering and analysis can continue, and establishing and applying techniques to use the information to project global energy demand for industry (as a function of economic conditions, demographic variables, technology choice, and policy).

The specific outcomes include:

- Completion of a major global assessment of energy efficiency in industry, with a focus on iron and steel, cement, and pulp and paper.

- Establishment of an international network of collaborators on industrial energy efficiency, including governmental representatives, academic researchers and analysts, and technical staff of the major energy-consuming industries in many nations.

Both the U.S. Department of Energy and the U.S. Environmental Protection Agency have become interested in this work and have funded several follow-on research projects as a result of this LDRD effort.

Accomplishments

Data Collection and Analysis

We collected and created a database of key structural data (output, energy, and economic data) to understand the drivers of industrial energy demand. The database covers six industrial subsectors (iron and steel, aluminum, building materials, chemicals, pulp and paper, and petroleum refining) and over 25 countries, with data coverage levels varying by sector and country. Database development is expected to continue using follow-on funding from related projects.

In addition to this database, we created and electronically catalogued an extensive library on industrial energy-demand information.

We prepared a summary report that focuses on the development and uses of this database to analyze the drivers of industrial energy use (see LBNL-42390). This report is currently under final review and will be available on the World Wide Web in the near future. Figure 1 from the report shows historical trends in energy intensity in iron and steel production for selected countries from the database. As the figure indicates, intensity is generally lower for industrialized countries but has dropped rapidly in China because of the introduction of newer technologies.

Additionally, we completed several preliminary analyses using existing data. One preliminary analysis we conducted, which focused on understanding current trends in industrial energy demand in China, found that energy requirements to produce a unit of raw material are still 20% to 40% higher than those in industrialized countries. Other studies soon to be published will focus on several key developing countries (also including China) and look in greater detail at the structure and drivers of steel and cement energy use.

As a result of the data collected in this project, LBNL is taking a leading role in developing methodology and parameters for energy-demand scenarios. We expect that such scenarios will be used by the Intergovernmental Panel on Climate Change, as well as by regional and national policymakers, to assess
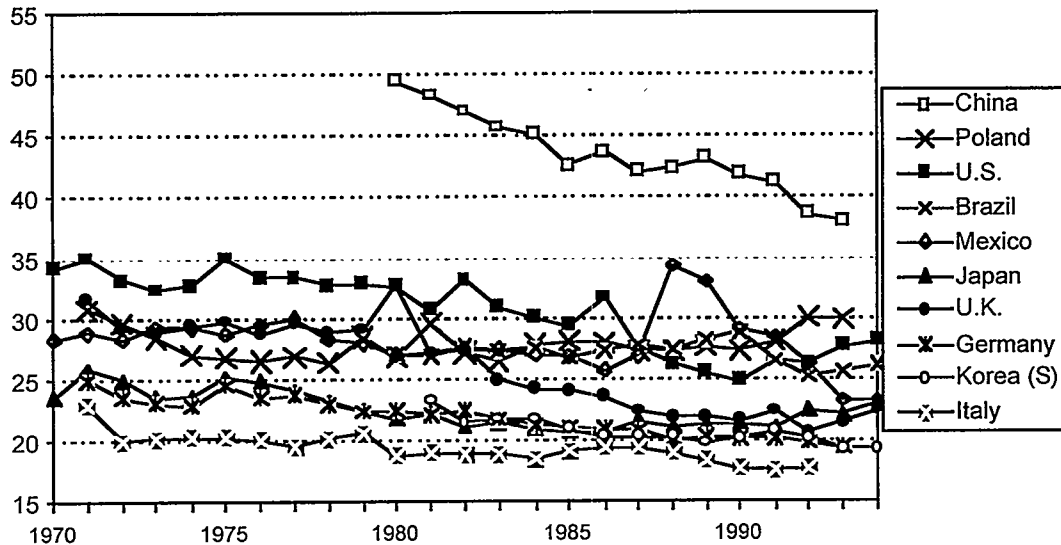
Figure 1. Energy intensity trends for iron and steel production (1971–1994).

policies and measures intended to reduce energy use and greenhouse-gas emissions. In addition, LBNL is developing and applying a number of analytic tools (e.g., decomposition analyses, best practice and international comparisons, and energy conservation supply curves) to better understand energy-demand trends in the industrial sector. (For a summary of project reports, see list of publications.)

Publications

M.D. Levine and L. Price, "The Role of Energy Efficiency in Reducing Growth in Global Energy Use and Greenhouse Gas Emissions: A Regional and Sectoral Analysis," Proceedings of ABARE Outlook '97 Conference (February 4–6, 1997).

M.D. Levine, L. Price, and J. Sinton, "Reducing Growth in Global Energy Use and Greenhouse Gas Emissions: A Regional and Sectoral Analysis of Energy Efficiency Opportunities," Proceedings of World Energy Council Asia-Pacific Forum (April 22–24, 1997).

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N. Martin, E. Worrell, J. Bode, A. Sandoval, and D. Phylipsen, "Industrial Energy Efficiency Policies: Understanding Success and Failure," LBNL-42368; Workshop Proceedings, Utrecht, The Netherlands (June 11–12, 1998).

L. Price, "Industrial Energy End-Use Demand Analysis," Proceedings of Asia Pacific Research Centre (1998).

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E. Worrell, L. Price, N. Martin, J. Farla, and R. Schaeffer, "Energy Intensity in the Iron and Steel Industry: A Comparison of Physical and Economic Indicators," *Energy Policy* 25, 7–9 (1997).

E. Worrell, L. Price, N. Martin, J. Farla, and R. Schaeffer, "International Energy Efficiency Comparisons and Policy Implications in the Iron and Steel Industry," Proceedings of European Council for Energy-Efficient Economy, Summer Study on Energy Efficiency in Industry (July 1997).

Assessment of Electricity Reliability Simulation Under Restructured Markets

Principal Investigators: Chris Marnay and Mark Levine

Project No: 98037

Project Description

The objective of this project is to study the modeling and computational requirements needed to ensure power system reliability in restructured electricity markets.

The electrical utility industry is entering an era of dramatic change all over the world. The current United States framework of territorially defined, investor or publicly owned utilities with captive customers and clear control of the power system will be replaced by a competitive commodity market with open customer access to energy suppliers, a publicly controlled but mixed publicly and privately owned transmission system, and traditionally franchised and regulated local distribution service. Many organizational variations are likely within this new structure, but responsibility for reliability, which has historically fallen on utility companies, is expected to fall on a new institution: the independent system operator (ISO). Approximately ten ISOs are currently being developed in the United States under direct regulation by the Federal Energy Regulatory Commission (FERC). Because each ISO operates with as yet unspecified authority over its transmission system, reliable service can be achieved only through close coordination of these heterogeneous generators. Tools and practices for ensuring reliability must be examined to ensure that (1) market structures and operational practices are set up by ISOs and regulators so that generators and other contributors to system reliability have incentives to contribute to a reliable system, (2) instability of new markets does not invade the physical power system, and (3) real-time control of the power system is not vulnerable to physical or cyber disruption.

Development of software tools will be necessary to efficiently and seamlessly achieve optimal levels of reliability in the overall electrical system. As our initial step, we will conduct a systematic study to identify capabilities and limitations of the methods and software currently used to ensure reliable

electrical service. Given the complex choices and time limits involved in this problem, analysis of supercomputing applications may be necessary.

Accomplishments

Progress on evaluation of existing tools has taken diverse forms:

- A bibliographic database of work in the power system reliability has been commenced.

- A review was conducted of existing operations simulation models. A promising graphically optimal power flow-based model developed at the University of Wisconsin was acquired and installed at LBNL. With this model, analysis of the entire Western States Coordinated Council region (covering most of the western U.S., Canada, and parts of Mexico) is possible.

- A paper has been drafted that addresses the problem of ensuring power system reliability while promoting high transmission system utilization in a restructured electricity market.

As part of the Consortium for Electric Reliability Technology Solutions (CERTS), this project involves joint research with partners from academia, the private sector, and other national laboratories. Further, through foreign visits to LBNL, linkages with two potential foreign partners have been established.

Publications

T. Gómez, H. Grønli, and C. Marnay, "Electric Power System Reliability Under Competitive Markets: What is New?" (paper in progress)

Virtual Building Laboratory

Principal Investigators: Stephen Selkowitz, Stephen Lau, Jr., and Nancy Johnston

Project No.: 97013

Project Description

The goal of this project is to develop the first operational module of the Virtual Building Laboratory, a suite of tools that will serve as a

building science research testbed and as a prototype for design tools of the future. The computational engine for the first module is Radiance, a lighting simulation tool using ray tracing, previously developed by the Environmental Energy Technology Division (EETD) staff.

Radiance produces physically accurate renderings of the luminous environment in buildings by accurately modeling the effects of lighting and surface interreflections. Although Radiance generates accurate renderings, the amount of computation required has precluded interactive decisionmaking or virtual walkthroughs in real time. This project attempts to achieve real-time frame rates by parallelizing the Radiance computations and also by developing a system of pixel reuse. We plan to reduce the amount of computation required to generate each frame by exploiting the frame-to-frame coherency during real-time walkthroughs. We will also explore the feasibility of having a remote user interactively control and view the visualization sequence at a location remote from the NERSC T3E.

The eventual goal of the project is to allow a user to explore all luminous aspects of a virtual space in a building, using an appropriate input device, without having to stop and run different programs at different points. By achieving this rapid frame rate and interactivity through optimization, Radiance will be useful for building design, for other industrial applications (e.g., Federal Aviation Administration), and for providing the tools and techniques needed to better serve NERSC remote users.

Accomplishments

A multidivisional and multidisciplinary team was formed between NERSC and the EETD for the project. One of the first tasks was to characterize the existing Radiance package to determine its performance. We investigated different methods of decreasing the amount of computation required to generate each frame. One area that we explored was active pupil tracking. By determining where the user was gazing, we hoped to greatly reduce the number of calculations required. Unfortunately, we determined that pupil tracking technology would not meet our needs at this time.

The ray-calculation portion of Radiance was parallelized onto the nodes of a T3E, using message passing interface technology. We have also ported this parallelization effort to a Silicon Graphics Origin 2000 multiprocessor machine. The NERSC remote-

visualization server was used as the front end to display the rendered images and as a user interface. A prototype user interface for controlling the user's eye position and direction-of-view was also developed and used. Although the parallelization of the ray-tracing portion of Radiance decreased the amount of time required to calculate each frame, it was still not enough for interactive rates. We developed a point cloud method for pixel reuse and tested it out with the parallelized portion of Radiance. The pixel reuse method was run on the remote visualization server, communicating with the NERSC T3E to determine which pixels need to be recalculated in each frame. For remote viewers, we are developing a method of utilizing the pixel change information to reduce the amount of bandwidth being sent over a network.

Using 64 nodes on the T3E, images are now rendered 40 times faster, and images can be displayed on a client machine every four seconds. For the first time, remote users can interactively control Radiance and display the resulting images on a workstation (Figures 1–2). This capability was demonstrated at Supercomputing '98 using the NERSC T3E and a graphics workstation on the show floor in Orlando, Florida.
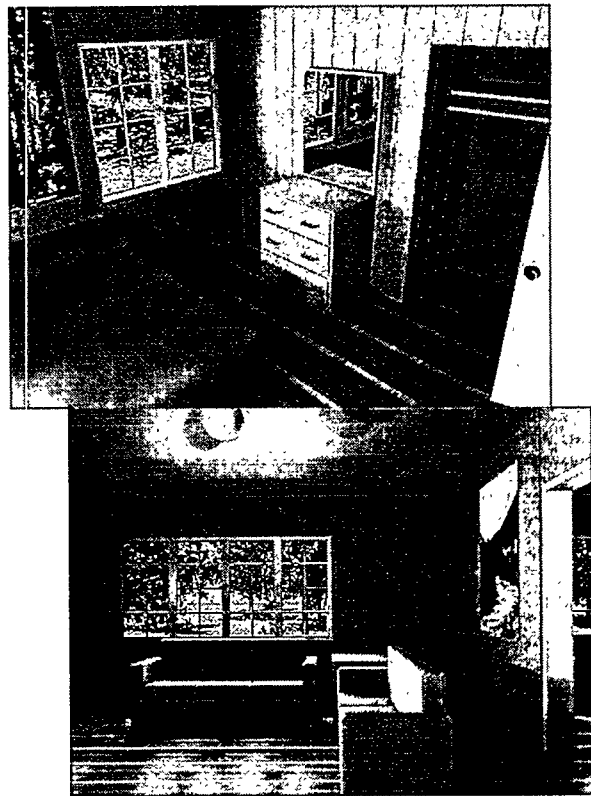
Figures 1–2. Generated with Radiance on the NERSC T3E showing two views of a cabin.

The principal investigators would like to acknowledge the participation of the following team members: David Robertson, Kevin Campbell, Charles Ehrlich, Kenneth Revzan, Shaheen Tonse, and Nancy Brown.

Publications

S. Lau, K. Campbell, and D. Robertson, "Parallelization of Radiance for Real-Time Interactive Lighting Visualization Walkthroughs" (presented at Supercomputing '98 poster session).

Life Sciences Division

Genomic Approaches to Understanding Cell Genotype and Phenotype

Principal Investigators: Judith Campisi, Paul Kaufman, and Kunxin Luo

Project No.: 98017

Project Description

Cell phenotype is defined by all genes expressed in a particular cell under a specific biological circumstance. Until recently, it has been impossible to know how external or internal stimuli alter the cell phenotype—or pattern of gene expression—to any degree of completion. Recent advances in genome research, however, make it possible to embark on an unprecedented, genomic-scale approach to defining and understanding cell phenotype.

This project studies genomic-scale approaches to biological questions that would otherwise be unanswerable by conventional molecular-biological techniques. To do so, we proposed to establish a cell genotyping/phenotyping core capability. We seek to acquire specialized equipment, develop streamlined procedures, and tailor state-of-the-art techniques to specific biological problems. During the two years of this project, we will implement two technologies: (1) DNA sequencing for gene identification and vector verification, as well as for complete gene-expression profiling (sequence-based gene profiling (SAGE) analysis); and (2) hybridization to microarrayed DNA and cDNA sequences, principally for analyzing gene-expression patterns.

Our long-term goal is to establish the technology for high-quality and highly competitive DNA sequencing and gene expression profiling, and to continue to develop the rapidly evolving, state-of-the-art methods for applying genomic-scale approaches to biological problems.

Accomplishments

The initial work in FY98 was to acquire most of the highly specialized equipment needed. This equipment included ABI-377 and 373 automated DNA sequencers, a Bio-Rad Cyclone imager, several thermocyclers and related equipment, and computer hardware and software for data management and image analyses. In addition, we have also hired a cell genotyping/phenotyping manager (Y. Zou), a part-time molecular biologist (G. Dimri), and a full-time sequencing assistant (C. Fong).

We have established and optimized individual plasmid-sequencing procedures, and, since November 1998, have achieved full sequencing capability. In addition, we have established the methodology for SAGE. SAGE entails constructing highly specialized cDNA libraries and sequencing several thousand library clones. The sequencing phase of this technology is currently underway.

We are also currently establishing and evaluating gene-expression profiling methods using filter hybridization. We have established ties with commercial suppliers of micro-arrayed cDNA filters, standardized the cDNA labeling and hybridization protocols, and acquired the imaging hardware and computer software for detecting and analyzing the hybridization signals. We are currently optimizing conditions for maximizing resolution and reproducing the hybridization signals.

ALS Protein Microcrystal Diffraction Camera

Principal Investigator: Robert Glaeser

Project No.: 97035

Project Description

The objective of this project is to define advances in instrumentation and research protocols that improve the quality of the diffraction data collected from protein microcrystals. We have collected full data sets that demonstrate the effectiveness of reduced x-ray beam size, matched as well as possible to crystal size when the crystal volume is extremely small. We

have also established quantitative guidelines for x-ray exposures suitable for data collection, taking into consideration the important limitation associated with radiation damage. We thus have been able to complete our primary goal—to obtain preliminary data that can be used in support of one or more research proposals for expanded operation of protein crystallography facilities at the Advanced Light Source (ALS).

Accomplishments

We obtained microcrystals of mutant forms of bacteriorhodopsin and wild-type bacteriorhodopson using a technique for crystallization in a lipidic cubic phase. We collected data on the F219L and D85S mutants at 0.25-nm resolution using the 100-μm collimator and the long-working-distance microscope on Beamline 5.0.2 (optics described in the last annual LDRD report). Our effort was supported by the Macromolecular Crystallography staff, especially C. Cork.

We also obtained basic calibration data by using an experimental microfocus diffraction camera set up by the Experimental Systems Group (H. Padmore and A. McDowell) on Beamline 7.3.3. We demonstrated the ability to record diffraction patterns to better than 0.2-nm resolution with a wide (1:200) band pass monochromator; we established quantitative values for the exposure levels (photons/square micrometer) suitable for collecting data from microcrystals; and we obtained quantitative data on the gradual destruction of the crystal due to radiation damage.

We are preparing data for future reports on the development and application of microdiffraction technology with the wide band pass mirrors and on structural results obtained from the mutant bacteriorhodopsin proteins.

Publications

ALS Experimental Systems Group; ALS Macromolecular Crystallography Facility, and LBNL Life Sciences Division/Physical Biosciences Division Protein Microcrystal Project; "Microfocus Diffraction Experiments with Protein Microcrystals," poster presented at meeting of ALS Users' Association (October 1998).

R.M. Glaeser, P. Walian, M. Facciotti, and S. Rouhani, "Microfocus Diffraction Experiments with Protein Microcrystals," poster accepted for meeting of Biophysical Society (February 1999).

Analysis of DNA Damage-Sensitivity of Yeast Mutants Lacking Chromatin Assembly Proteins

Principal Investigator: Paul Kaufman

Project No.: 96039

Project Description

This project focuses on the protein complex chromatin assembly factor-I (CAF-I), an evolutionarily conserved factor that assembles nucleosomes in a manner linked to DNA replication *in vitro*. This project studies the relationship between CAF-I activity and radiation sensitivity in the yeast *Saccharomyces cerevisiae*, which can be studied genetically as well as biochemically.

Many advances in cancer research depend on understanding how eukaryotic chromosomes are assembled and protected from damage. Earlier work showed that human CAF-I will assemble nucleosomes on DNA templates that undergo nucleotide excision repair. Therefore, the initial phase of this project has tested the role of CAF-I in DNA damage sensitivity *in vivo*. Current experiments are underway to understand the biochemical changes in chromatin caused by defects in CAF-I function.

Accomplishments

We first demonstrated that cell extracts from the budding yeast *Saccharomyces cerevisiae* contained a biochemical activity that would perform DNA replication-linked nucleosome assembly, as had been previously observed in humans, *Drosophila*, and *Xenopus*. Detection of this activity allowed for biochemical purification of the yeast factor.

By amino-acid sequence analysis of purified protein, we have identified the genes encoding each of the three yeast CAF-I subunits, termed *CAC1*, *CAC2*, and *CAC3* (chromatin assembly complex). Identification of these genes demonstrated that each is homologous to its human counterpart and allowed for construction of yeast strains lacking individual or multiple CAF-I subunits.

We have established that CAF-I plays a role in protecting the genome from certain types of DNA

damage. Specifically, we quantitatively assessed the degree of sensitivity to different DNA damaging agents, using cells lacking each of the CAF-I subunits. Ultraviolet (UV) light (forming thymine dimers and other photoproducts) and x-ray irradiation (causing double-strand breaks) were tested. Interestingly, mutations in all CAF-I subunits result in increased sensitivity to ultraviolet radiation but not to x-rays. These data suggest that nucleosome assembly by CAF-I is activated by some but not all forms of DNA damage.

To determine which repair process involves CAF-I *in vivo*, we used double and triple mutants involving *cac1*Δ and deletions of yeast repair genes to show that the *CAC1* gene falls into the *RAD6* epistasis group with respect to its UV-repair defect. Double mutants involving *cac1*Δ and either *rad6*Δ or *rad18*Δ were no more UV-sensitive than the corresponding *rad*Δ · mutants alone. In contrast, double mutants involving *cac1*Δ and the excision repair mutants *rad1*Δ or *rad14*Δ showed increased UV-sensitivity, as did double mutants involving *cac1*Δ and deletions of members of the *RAD51* recombinational repair group. These and other findings suggest that CAF-I facilitates post-replicative DNA repair mediated by the *RAD6* pathway.

These *in vivo* experiments suggest that nucleosome formation in *cac* mutants may be insufficient for full protection of cellular DNA from UV damage. We currently do not have a clear understanding, however, of the biochemical defects in chromatin made in the absence of CAF-I and why such chromatin is less well repaired. Therefore, we have been developing methods to biochemically isolate sufficient quantities of chromatin from yeast to allow for analysis of protein components. Because the role of CAF-I in chromatin formation is most clearly defined at telomeres, we have concentrated our efforts on isolation of telomeric chromatin. We are able to isolate telomeric chromatin free of internal chromosomal DNA, and we have been comparing the protein composition of these preparations with preparations made from various mutant strains lacking CAF-I and other known chromatin components.

Publications

P.D. Kaufman, R. Kobayashi, and B. Stillman, "Ultraviolet Radiation-Sensitivity and Reduction of Telomeric Silencing in *Saccharomyces cerevisiae* Cells Lacking Chromatin Assembly Factor-I," *Genes Dev.* 11, 345–357 (1997).

A. Verreault, P.D. Kaufman, R. Kobayashi, and B. Stillman, "Nucleosomal DNA Regulates the Core-Histone-Binding Subunit of the Human Hat1 Acetyltransferase," *Current Biology* 8, 96–108 (1998).

P.D. Kaufman, J.L. Cohen, and M.A. Osley, "Hir Proteins Are Required for Position-Dependent Gene Silencing in *Saccharomyces cerevisiae* in the Absence of Chromatin Assembly Factor-I," *Mol. Cell. Biol.* 18, 4793–4806 (1998).

J.C. Game and P.D. Kaufman, "Role of *Saccharomyces cerevisiae* Chromatin Assembly Factor-I in Repair of Ultraviolet Radiation Damage *in vivo*," *Genetics* (in press).

Studies of the Expression of Trinucleotide-Repeat Sequence-Binding Proteins (TRIPs [Renamed CAGERs]) in the Brain

Principal Investigator: Yoshinori Kohwi

Project No.: 97016A

Project Description

This LDRD project arises from the discovery of a new class of mutations—the expansion of trinucleotide repeats—in the genes responsible for several genetic disorders. This discovery has triggered the search for the mechanisms of these mutations in humans. These mutations include the trinucleotide-repeat expansion of (CGG)n in the mutant gene responsible for the inherited mental retardation disorder fragile X syndrome (CAG)n in the gene responsible for myotonic dystrophy (Dystrophia Myotonica [DM], an autosomal dominant neuromuscular disease); the androgen receptor gene of X-linked spinal and bulbar muscular atrophy, a rare motor neuron disorder (SBMA or Kennedy's disease); the gene responsible for Huntington's disease (HD); and the genes responsible for spinocerebellar ataxia type1 (SCA1), hereditary dentatorubral-pallido-luysian atrophy (DRPLA), and Machado-Joseph disease. In many of these conditions, severity and/or age of disease onset is determined by the number of repeating units. Although the expansion of trinucleotide repeat

sequences has been associated with genetic disorders, it is not known how trinucleotide repeats expand or how this expansion causes disease

Huntington's disease (HD) is an autosomal dominant genetic disorder, estimated to affect approximately 1 in 10,000 individuals. It is characterized by progressive neurodegeneration resulting in involuntary movements, and cognitive decline and dementia as a result of neuronal cell death, particularly in the nucleus caudate and putamen of the basal ganglia. DRPLA is an autosomal-dominant neurodegenerative disorder characterized by a varying combination of progressive myoclonus, epilepsy, ataxia, choreoathetosis, and dementia. It is particularly prevalent in Japan.

Recent work in transgenic mice production and analysis indicates that the toxicity expression by polyglutamine in expanded trinucleotide repeat genes may be sufficient to generate a mouse model of such diseases. In particular, HD-model mice provide an intriguing mouse model, in which the introduced-HD genes are ubiquitously expressed and the features of the movement disorder and the complex HD phenotype are reproduced, although specific neuronal cell death in HD mice is not apparent.

The neuron-selectivity of cell death by triplet disease gene products may suggest the involvement of other factors in the brain. To understand the mechanism of neurodegenerative diseases resulting from trinucleotide-repeat sequence expansion, we searched for other factors to interact with trinucleotide repeat sequences. Previously, we detected and purified two proteins responsible for single-stranded (ss)-(CAG)n repeat-binding activity in a mouse brain. The (CAG)n-repeat-sequence-binding proteins bind specific subsets of single-stranded trinucleotide-repeat sequences, including ss(CGG)n repeats. We named these two proteins TRIP-1 and TRIP-2 (where TRIP represents trinucleotide repeat-binding protein). Recently, however, we noticed that there are 6 different proteins with identical names (TRIPs). Therefore, to avoid confusion, we decided to rename these proteins CAGERs (CAG-element recognizing proteins).

We hypothesize that CAGER expression is correlated with cognitive ability in neurogenetic disorders and age-dependent dementia. We propose to find out whether there is altered expression of CAGERs in brains that have neurodegenerative diseases, including HD.

Accomplishments

During the previous year, we isolated cDNAs from mouse brains, encoding two homologous proteins that preferentially bind single-stranded (ss)(CAG)n and ss(CGG)n repeats. These proteins, designated as CAGER-1 and CAGER-2, are predominantly expressed in mature neurons, but not in fetal brains in the central nervous system (CNS). The expression of these two proteins increases in parallel postnatally in the brain. CAGERs are found exclusively in cytoplasm and bind native growth associated protein (GAP)-43 mRNA *in vitro*, suggesting that these are neuronal mRNA binding proteins. The biological function of CAGERs was tested in PC12 pheochromocytoma cells that are known to differentiate into sympathetic like-neurons in response to nerve growth factor (NGF). Overexpression of CAGER-1 into PC12 cells promotes neurite outgrowth and induces neuronal differentiation in the absence of NGF. The transfected CAGER-1 in PC12 cells was detected in growth cones as well as in the neuronal fibers. Localization in growth cones and the mRNA binding activity of CAGERs suggest that, at least in culture cells, CAGERs may bind mRNA *in vivo* and transport or stabilize mRNA species essential for neurite outgrowth.

Certain mRNAs are known to localize not only in dendrites but also in axons, yet the significance of mRNA localization in axons in vertebrate animals had been questioned. Now, we have succeeded in raising specific antibodies against CAGER-1 and CAGER-2. Using these antibodies, we found that neuronal mRNA binding proteins (CAGERs) localize in axons in CNS *in vivo* and maintain neurites without neurotrophic factors in cultures. Neuronal mRNA binding proteins in axons may have an active role for neuronal network formation in CNS. The immunostaining of CAGER-1 and CAGER-2 in mouse brain *in vivo* reveals that the strong signals of CAGER-1 and CAGER-2 were detected in the cell bodies of most neurons, as well as in their fibers, at a different level in different areas. The strong staining of CAGER-1 is observed in fibers of caudate/putamen, anterior commissure, corpus callosum, fornix, and internal capsule. The distributions of CAGER-1 and CAGER-2 in the neuronal fibers support the idea that CAGERs may play a role in mRNA transportation in neurons *in vivo*. These data suggest that CAGERs may be important for maintaining the neuronal network CNS, not only in dendrites but also in axon fibers.

Publications

H. Yano-Yanagisawa, B.-E. Wang, I. Ahmad, J. Zhang, T. Abo, J. Nakayama, and Y. Kohwi, "(CAG)n and (CGG)n RNA-Binding Proteins (CAGERs), Expressed in Mature Neurons, Promote Neurite Outgrowth" (submitted).

B.-E. Wang, I. Ahmad, J.-Z. Zhang, W. Meyer-Ilse, H. Yano-Yanagisawa, K. Krempen, and Y. Kohwi, "Neuronal RNA Binding Proteins, CAGERs, Localized Not Only in Dendrite but Also in Axon in CNS and Migrate to Outer Core of Growth Cone in Cultures" (to be submitted).

Isolation and Characterization of SATB1-Bound Sequences In Vivo

Principal Investigator: Terumi Kohwi-Shigematsu

Project No.: 97016B

Project Description

The higher order structure of eukaryotic chromosomes consists of independent loop domains that are separated from each other by the attachment of specialized genomic sequences (matrix attachment region, or MAR) onto the nuclear matrix. Such loop domain structures are not only important for compacting genomic DNA, but they also presumably play a role in regulating DNA function, including replication, recombination, and transcription. In fact, much evidence has been accumulated to show that active replication and transcription processes are undertaken at the site of the nuclear matrix, suggesting that MARs could be important targets for the regulation of DNA function. MARs have been identified to date on the basis of their in vitro binding to the nuclear matrix. Therefore, an important question still remains as to what type of genomic sequences actually anchor genomic DNA onto the nuclear matrix in vivo. Once such a series of loop attachment sequences is analyzed, one could then address what makes these sequences attach to the nuclear matrix and the consequent biological roles. Such information will promote understanding of the three-dimensional utility of linear genomic sequences.

We previously cloned a T cell factor, SATB1, which is a cell-type-specific MAR-binding protein predominantly expressed in thymocytes. SATB1 binds specifically to a particular region (a base unpairing region, or BUR) typically found in MARs. BURs (which typically span 100–300 bp) have a very high propensity to unwind, and they represent key structural elements of MARs. SATB1 and anti-SATB1 antibodies can be used to isolate BUR sequences that bind to SATB1 in vivo to examine their biological function.

Accomplishments

We devised a method to clone genomic sequences that bind to SATB1 in vivo. Using this method, we isolated a set of genomic sequences from Jurkat cells and thymocytes, and demonstrated that a MAR-binding protein binds to BURs in vivo at the bases of chromatin loops. These experiments unambiguously demonstrated for the first time that a specific set of genomic DNA sequences are anchored onto the nuclear matrix and bound in vivo to a cell-type-specific MAR-binding protein. Also, we found that anchoring of specific genomic sequences onto the nuclear matrix is cell-type dependent, demonstrating that the three-dimensional organization of chromatin is also cell-type specific. We have established a method for visualization of single copy loci by in situ hybridization using short sequences as probes. Using this method, we examined the localization of a genome sequence that is bound to SATB1 in vivo in thymocytes before and after T cell activation. We found that upon activation, the sequence becomes anchored onto the nuclear matrix in vivo; before activation, it remained detached. Therefore, the nuclear localization of specific DNA sequences that SATB1 binds to is subject to change in response to T cell activation.

For some mouse genomic sequences that are bound to SATB1 in vivo in thymocytes, we have identified genes located nearby. We are in the process of studying transcriptional activity of these genes in wild type and SATB1 knockout animals. We have also established a quick method to clone BUR sites from P1 and BAC clones. Using this method, we have analyzed the entire 1 Mbp region of the mouse cytokine gene cluster region. Such a quick method for identification of BUR sites is potentially useful as an annotation of genomic sequences. Some BURs are found to be clustered in a region that potentially borders cell-type-specific genes and constitutive

genes. We plan to examine the biological function of these BURs in the future.

Publications

I. deBelle, S. Cai, and T. Kohwi-Shigematsu, "The Genomic Sequences Bound to Special AT-Rich Sequence-Binding Protein 1 (SATB1) In Vivo in Jurkat T Cells are Tightly Associated with the Nuclear Matrix at the Bases of the Chromatin Loops," *J. Cell Biol.* **14**, 335–348 (1998).

S. Cai and T. Kohwi-Shigematsu, "Intranuclear Relocalization of Matrix Binding Sites during T Cell Activation Detected by Amplified Fluorescence In Situ Hybridization," *Methods* (in press).

Localization of Proteins in Hydrated, Whole Cells Using Biological X-Ray Microscopy at ALS

Principal Investigator: Carolyn Larabell

Project No.: 98038

Project Description

Soft x-ray microscopy provides high spatial resolution (40–50 nm) images of thick, hydrated samples like whole cells. We recently demonstrated the power of using silver-enhanced, gold-labeled antibodies to localize proteins in hydrated, whole cells at unsurpassed resolution. The goal of this project is to exploit these developments in a variety of biological applications and to expand our technical capabilities beyond the present state-of-the-art microscopy.

To examine the distribution of specific proteins using x-ray microscopy, we modified immunolabeling protocols previously used for fluorescence and electron microscopical analyses. We used a commercially available probe, FluoroNanogold®, that is tagged with fluorescein molecules for visualization in fluorescence microscopy and 1.4 nm Nanogold® particles that readily pass through permeabilized cell membranes. We then coated the gold particles with silver until the aggregates were large enough to visualize in the x-ray microscope. Using this approach, we demonstrated specific labeling of cytoplasmic and nuclear proteins. We will use this labeling protocol to compare the distribution of proteins in normal versus tumor cells at a level of resolution that is five times higher than that possible with light microscopy.

Accomplishments

We recently developed a technique for examining the distribution of proteins using x-ray microscopy. To enhance both the sensitivity and specificity of labeling, we devoted a significant amount of time to improving this labeling protocol. Once we were satisfied with the improved protocol, we were able to begin examining the distribution of several important nuclear and cytoplasmic proteins in human mammary epithelial cells. In each case, we examined the distribution of proteins in "normal" cells (S1) versus tumor cells (T4) and tried to determine whether these proteins move from the cytoplasm to the nucleus during tumorigenesis. We are also examining the distribution of these proteins at different stages of growth and proliferation. All of this work is still in progress, and our data is too preliminary to report at this time.

We also obtained our first stereo images of labeled proteins in cells using the x-ray microscope. Because we do not have a tilt stage, this involved extremely tedious manipulations. As a consequence, we performed these studies using dehydrated cells on electron microscopy grids rather than our standard hydrated cells grown on thin membranes. In any event, we were able to collect several data sets that clearly demonstrate the power of stereo imaging to discern information regarding relative positions of proteins in the x-z direction. Collecting stereo images will significantly increase the amount of information we can obtain from the labeled cells.

Publications

W. Meyer-Ilse, D. Hamamoto, S. Lelievre, A. Nair, C. Larabell, "High-Resolution Antigen Localization Using Soft X-Ray Microscopy" (in preparation).

Analysis of Cellular Factors That Activate Transcription from Major TGFβ-Responsive Element in Plasminogen Activator Inhibitor Type-1 Gene

Principal Investigator: Kunxin Luo

Project No.: 98018

Project Description

The TGFβ family of cytokines has a wide range of biological functions in many cellular processes including tumor suppression, extracellular matrix production, embryonic development, hematopoiesis, and immune and inflammatory cell responses. How does a single molecule initiate such diverse and complex cellular events? Are they mediated by different signaling pathways? The goal of this proposal is to characterize the signaling pathway of TGFβ receptors leading to extracellular matrix production at the level of transcriptional activation. This proposal will allow for the identification and purification of cellular transcription factors that activate specific gene expression in response to TGFβ stimulation.

The signaling receptors for TGFβ include TβRI and TβRII, the type I and II receptors for TGFβ, which are members of the first known transmembrane serine/threonine kinase family and share 40% homology between their kinase domains. TGFβ1 binds directly to TβRII, allowing the formation of heteromeric complexes of TβRI and TbRII, and the transphosphorylation of TβRI by the constitutively active TβRII. It has been suggested that phosphorylation of TβRI activates its kinase activity and allows it to phosphorylate downstream substrates such as Smad2 and Smad3. The phosphorylated Smad proteins then translocate to the nucleus and subsequently activate downstream events. However, little is known about how the Smad complex activates the transcription of TGFβ-responsive genes. Recently, Drosophila Smad protein was found to bind to a DNA sequence present in the promoter region of Dpp-responsive genes. This finding suggests that Smad proteins could activate transcription by binding directly to TGFβ responsive elements.

We decided to analyze the signaling pathway leading to transcriptional activation of TGFβ-responsive genes using the PAI-1 promoter, because it has been well documented that TGFβ stimulation results in a fifty-fold induction of PAI-1 gene transcription. The promoter region of the PAI-1 gene has been well characterized, and a major TGFβ-responsive region has been mapped to a 258 bp sequence between –804 and –546 upstream of the initiation site. Although the sequence contains an AP-1-like motif, cellular factors that may interact with this region and activate transcription have not been identified. By overexpressing dominant negative and constitutively active Smad mutants in some cell lines, Smad proteins have been shown to be involved in the activation of PAI-1 transcription. However, the molecular basis of PAI-1 activation by Smads is not clear. Since human Smad4 shares a considerable homology with Drosophila Smad, and Drosophila Smad can bind DNA directly, we hypothesize that human Smad4 may also activate PAI-1 transcription by direct binding to specific sequences in the PAI-1 promoter. Using electrophoretic mobility shift assays (EMSA), we will investigate the mechanism by which Smad proteins activate PAI-1 transcription.·

Accomplishments

We have expressed in and purified Smad2, Smad3, and Smad4 proteins from E. coli and tested their ability to bind to specific sequences (–674 to –655) in the PAI-1 promoter in an EMSA assay. Both Smad3 and Smad4 caused a mobility shift of the labeled DNA probe. In contrast, Smad2 did not bind to this DNA fragment. This result clearly demonstrates a functional difference between Smad2 and Smad3, although the two proteins showed more than 90% sequence identity.

This region of PAI-1 promoter contains a GTCTGGAC motif (site 1) that is very similar to the optimal Smad3 and Smad4 binding sequence obtained by a PCR selection process (GTCTAGAC), as well as an AP-1-like element (GAGTCAG) (site 2) that differs from the typical AP-1 site by one nucleotide (TAGTCAG). To determine which motif is recognized by Smad3 and Smad4, EMSA analysis was carried out with mutant DNA probes that contained mutations at either site. Interestingly, Smad3 and Smad4 bound to both mutant probes. However, the binding of Smads to a wild-type probe containing both sites was stronger and showed a greater shift in mobility. This result suggests that this region of PAI-1 promoter contains two Smad binding sites that can interact with

at least two Smad molecules simultaneously. The two binding sites may coordinate to increase the affinity of Smad proteins to PAI-1 promoter.

To determine which domain in Smad3 and Smad4 is responsible for DNA binding, we made truncations of Smad3 and Smad4 and expressed them in *E. coli*. The amino terminal MH1 domain of both Smad3 and Smad4 showed DNA binding activity, whereas the C terminal part of the Smads cannot bind DNA.

Both sites were necessary for TGFβ-induced, Smad3- and Smad4-dependent activation of PAI-1 transcription. Contrary to a previously reported mechanism of action by Smads, transactivation of this part of the PAI-1 promoter by the Smads was mediated by the N-terminal domains of the Smads and did not require the C domains. Furthermore, oligomerization of Smad3, although not essential for direct DNA binding, markedly enhanced binding to the two Smad binding sites. Finally, a Smad4 mutation identified in a human pancreatic carcinoma that inactivates Smad4 signaling abolished the DNA-binding activity of Smad4, hence preventing transactivation of TGFβ-responsive genes. These results underscore the importance of the DNA binding ability of Smad4 in controlling cell growth and carcinogenesis.

Publications

S.L. Stroschein, and K. Luo (1998), "Cooperative Binding of Smad Proteins to Two Adjacent DNA Elements in the Plasminogen Activator Inhibitor-1 Promoter Mediates TGFβ-Induced, Smad-Dependent Transcriptional Activation" (submitted for publication).

Development of Novel Biological Targeted Therapies for Breast Cancer

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Principal Investigator: Ruth Lupu

Project No.: 97018

Project Description

The aim of this project was to design novel therapeutic strategies for the treatment of carcinomas that overexpress the erbB-2 oncogene product. ErbB-2 is a tyrosine kinase growth factor receptor, the

overexpression of which correlates with poor prognosis and poor overall survival in patients with invasive breast, prostate, ovarian, and lung carcinomas. In breast carcinomas, erbB-2 is overexpressed in 25–30% of the invasive phenotype and in 70% of ductal carcinomas *in situ*. Tumors that overexpress erbB-2 are a leading cause of death, making erbB-2 a critical target for developing beneficial therapy for a large number of cancer patients.

Using two independent, yet complementary, strategies, we developed (1) a leading peptido-mimetic agent (PM2) corresponding to the functional site of the erbB-2 protein sequence and (2) a battery of erbB-2 deletion mutants. We demonstrated that PM2 blocks erbB-2 auto-phosphorylation and selectively inhibits the growth of tumors by erbB-2-overexpressing cells in athymic nude mice. We also demonstrated that when the putative functional site of the erbB-2 receptor mutates, invasion and spreading of breast cancer cells cease.

Taken together, our data demonstrate that targeting the receptor (erbB-2) and/or the functional sites results in the inhibition of cell growth and blockage of metastasis *in vitro*. The advantage in developing these strategies is a direct targeting exclusively to cancer cells. Thus, we have developed a specific and efficient peptido-mimetic agent (PM2) that could be developed into one or more therapeutic drugs.

Accomplishments

Identification of ErbB-2 Peptido-Mimetic Agent (PM2)

The increasing number of newly discovered anticancer agents results from our understanding of the mechanisms of tumorigenesis rather than the random screening of molecules. We used a strategy to block erbB-2 activation rather than its expression. We developed a number of congers from the initial leading peptide and identified a highly specific conger of nine amino-acid peptide-mimetic to erbB-2 named PM2.

Blockage of HRG-Induced Phosphorylation of ErbB-2 Receptor

To characterize the PM2 blocking effects, we analyzed its ability to prevent tyrosine phosphorylation of erbB-2 receptor induced by HRG. We then used *in vivo* and *in vitro* tyrosine phosphorylation assays. In MDA-MB-453 cells, which express the erbB-2 receptors, PM2 inhibited the baseline, and HRG

stimulated levels of erbB-2 tyrosine phosphorylation by up to 96%. The specificity of PM2-blocking effects on erbB-2 tyrosine phosphorylation was confirmed by *in vivo* phosphorylation assays and immunoprecipitations with specific anti-erbB-2 antibodies. Results revealed that PM2 caused a marked decrease in the phosphorylation of erbB-2 tyrosine residues.

Inhibition of Anchorage-Independent Growth of ErbB-2-Overexpressing Cells

To determine the *in vitro* growth effects of MDA-MB-453 cells (which overexpress erbB-2), we learned that PM2 blocked the growth of breast cancer proliferation. Studies of PM2 inhibitory effects on erbB-2-overexpressing cells provide a new tool to elucidate the mechanisms of erbB-2 action and, more importantly, to elucidate a unique potential for anti-erbB-2 targeted therapy in human breast cancer.

Generation of ErbB-2 Receptor Deletion Mutants

To determine the critical importance of the functional site of the erbB-2 receptor, we developed a series of deletion mutants. All the designed deletions retained their proper reading frame to preserve the normal intracellular sequence and function. The mutants were characterized by restriction enzyme analysis and confirmed by direct sequence analysis. We are now in the final biological characterization of these mutants and will be in a position to determine their biological significance.

Signal Transduction and Cytoskeleton

Principal Investigator: Mohandas Narla

Project No.: 98019

Project Description

In this project, we have conducted research into new areas of cell and molecular biology: (1) the functional characterization of homologues of red-cell-membrane proteins in nonerythroid cells and (2) understanding the role of cytoskeleton in signal transduction and erythroid cell differentiation.

Functional Characterization of Homologues of Red-Cell-Membrane Proteins in Nonerythroid Cells

Recent studies from our group and a number of other groups have shown that homologues of the red-cell-membrane cytoskeletal proteins spectrin, ankyrin, and protein 4.1 are also present in a number of nonerythroid cells, including epithelial cells, fibroblasts, endothelial cells, and neuronal cells. At present, however, we have no knowledge of the function of these proteins in these cells. During the last ten years, our group has played a key role in defining the function of cytoskeletal proteins in the red-cell membrane, using biophysical, biochemical, and molecular biological approaches. We have recently shown that protein 4.1 is a component of the nuclear matrix, of Golgi membrane, and of centrosomes. During the first year of this project, we proposed to initiate a detailed characterization of different homologues of red cell protein 4.1R and begin the functional characterization of this protein family in nonerythroid cells, especially neuronal cells.

Understanding the Role of Cytoskeleton in Signal Transduction and Erythroid Cell Differentiation

Erythropoiesis, responsible for generation of 2.5-million red cells per second in humans, is an excellent system by which to study cell differentiation. Although the critical roles for the hormone erythropoietin and its receptor in erythroid differentiation have been well delineated, the downstream signaling pathways are yet to be defined. In particular, the potential role of cytoskeleton in the process has not been explored. We proposed to use a congenital disorder, the Diamond-Blackfan anemia, in which newborns have a complete lack of red-cell production, to explore the signal transduction process. We perform these studies because detailed exploration of the molecular basis for this congenital disorder has failed to document any abnormalities in either erythropoietin production or the erythropoietin receptor gene. It is therefore reasonable to postulate that the primary defect is in the signal transduction pathway. Obtaining preliminary data to validate our concepts will enable us to obtain funding from the National Institute of Health or DOE to build a new program for erythroid differentiation.

These research efforts fit very well with ongoing plans for the development of a postgenomics biology program at LBNL that entails integration of genomic and cell biology research. The proposed research entails the use of modern molecular biological

approaches, innovative microscopic strategies, and state-of-the-art cell-biological techniques.

Accomplishments

During the first year of LDRD funding, we made substantial progress in both of our proposed initiatives. We have cloned and sequenced the cDNA of three human homologues of red-cell protein 4.1R (4.1G, 4.1N, and 4.1B). The 4.1G gene product is ubiquitously expressed in all tissues, the 4.1N gene product is expressed in all neurons, and the 4.1B gene product is expressed predominantly in the brain. Having completed the detailed characterization of these three new human homologues of red-cell protein 4.1R, we are currently exploring the function of these proteins. In particular, we are focusing our efforts on defining the function of various protein 4.1 gene products in neuronal cells (in collaboration with S. Snyder's group at Johns Hopkins University) and in kidney epithelial cells.

The second research initiative we pursued involves the study of the congenital disorder, Diamond-Blackfan anemia. Because detailed exploration of the molecular basis for this congenital disorder has failed to document any abnormalities in either erythropoietin production or the erythropoietin receptor gene, we postulated that the primary defect is in the signal transduction pathway. Our collaborator, G. Tchernia, and his colleagues in France have extensive expertise in the study of this disorder. The gene responsible for lack of red-cell production has recently been localized to a 1.5-Mb region of chromosome 19. We have performed fine mapping of this region and have identified three candidate genes. We are currently defining which of these three genes are expressed in erythroid cells. We anticipate that in the very near future we will be able to identify the gene responsible for the lack of red-cell production in newborns.

Publications

M. Parra, P. Gascard, L.D. Walensky, S.H. Snyder, N. Mohandas, and J.G. Conboy, "Cloning and Characterization of 4.1G, A New Member of the Skeletal Protein 4.1 Gene Family," *Genomics* 49, 298–306 (1998).

L. Peters, H.G. Weier, L.D. Walensky, S.H. Snyder, M. Parra, N. Mohandas, and J.G. Conboy, "Four Paralogous Protein 4.1 Genes Map to Distinct Chromosomes in Mouse and Man," *Genomics* 54, 348–350 (1998).

L.D. Walensky, P. Gascard, M.E. Fields, S. Blackshaw, J.G. Conboy, N. Mohandas, and S.H. Snyder, "Immunophilin FKBP13 Interacts with a Novel Homologue of the Erythrocyte Membrane Cytoskeletal Protein 4.1," *J. Cell Biology* 141, 143–153 (1998).

Cryo-Electron Microscopy of Septins: Implementation of Cryotechniques at National Center for Electron Microscopy

Principal Investigator: Eva Nogales

Project No.: 98039

Project Description

The structural study (at the nanometer scale) of large protein complexes is possible only by electron microscopy. In particular, cryo-electron microscopy and low-dose techniques ensure the preservation of the biological sample and the fidelity of the images obtained from it. The objective of this proposal is to make use of the excellent technical capabilities of the National Center for Electron Microscopy (NCEM) at LBNL to study biological samples by cryo-preservation methods. The 200 KeV microscope with a field emission gun at the NCEM was to be equipped with a specimen cryo-holder and a dedicated anticontaminator. We would use low-dose software for recording images of frozen-hydrated samples of septin complexes. Septins are a class of proteins involved in cytokinesis in all cells from yeast to mammals. Essential to their function is the self-assembly of septins into fibers by a mechanism that is not yet understood. Structural information on the intact septin polymer will be essential for characterizing septin's mechanism of function. In addition, implementing of cryo-techniques at the NCEM will expand the capabilities of this facility to include the study not only of biological samples, but also of other organic samples (such as polymers) that are radiation sensitive.

Accomplishments

A cryo-holder and an anticontaminator, specially suited for the Philips CM200 electron microscope at the NCEM, were purchased from GATAN and

installed in the microscope. The cryo-holder and its workstation allow the loading of specimens at liquid-nitrogen temperature into the microscope and their study at this temperature. The anticontaminator guarantees a water-free environment around the very cold specimen during its observation. This anticontaminator can be retracted in and out of the electron path, while the cryo-holder is taken in and out of the microscope column with each experiment, leaving the normal operation of the microscope unaffected. This cryo-implementation has opened the possibility for the study of biological samples and other radiation-sensitive materials (Figure 1).

A low-dose software package from Philips has been implemented at the CM200. The software allows us to use the minimum electron dose required to find the sample, focus the image, and take a picture, hence eliminating unwanted irradiation of the sample and minimizing damage. This package is easy to use and therefore particularly suited for a user facility.
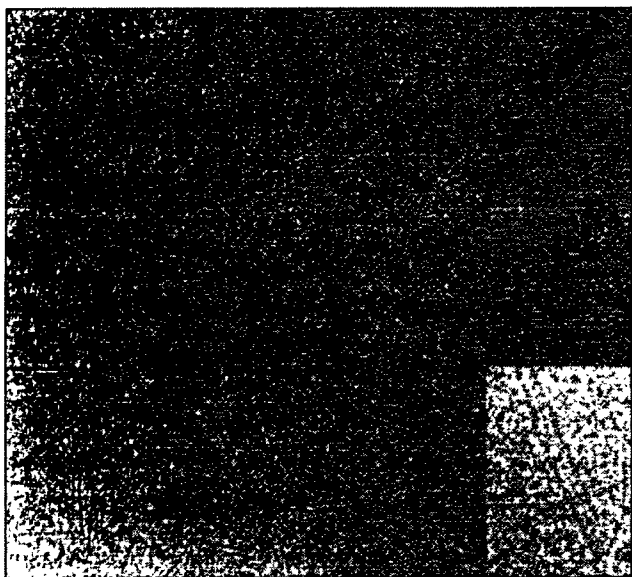
Figure 1. The new cryo-electron microscopy setup has been used for the last month to study the structure of septin filaments. The images show the presence of single and double filaments of different lengths in low-salt solutions of the septin complexes. A minimal unit length can be observed, indicating that this is the structural repeat formed by the four protein components of the septin complex.

Gene-Specific Biomonitoring to Assess Risk of Developing Environmentally Induced Leukemia

Principal Investigator: Maria Pallavicini

Project No.: 97020

Project Description

The increased incidence of hematological malignancies (e.g., leukemia) is a potential health risk associated with exposure to chemicals in contaminated groundwater, toxic sites, and atmospheric microenvironments. Epidemiological studies have established that exposure to benzene and radiation is associated with increased risk of acute myelogenous leukemia, non-Hodgkin's lymphoma, multiple myeloma, and other hematopoietic malignancies. Stem cells in the marrow are one of the populations involved in leukemogenesis. The primary goal of this study is to increase understanding of the genetic and functional alterations that occur in hematopoietic stem cells after environmental insults. We have utilized our expertise in stem cell biology, molecular cytogenetic analysis, and biomonitoring assays to identify the critical regions in the mouse genome for candidate tumor-suppressor genes that are relevant to leukemogenesis and that may be altered by environmental exposure.

Leukemogenesis is a multistep process in which a series of acquired genetic abnormalities predispose to myelodysplasia, which is often followed by clonal expansion of progenitor cells to generate excess blasts in the marrow and in peripheral blood. Non-random rearrangement of DNA sequence in human chromosome 5 occurs in approximately 35% of secondary leukemia (i.e., those induced by pesticides, radiation, and chemotherapy, etc.). We hypothesized that functional loss of genes located in human chromosome 5 may be an early event in leukemogenesis. We tested this hypothesis by quantifying DNA sequence loss from murine chromosomes 11 and 13, syntenous to the human chromosome 5 region, in stem cells from mice exposed to radiation. Specifically, we tested the hypothesis that exposure of cycling hematopoietic stem cells to leukemogenic environmental genotoxins will induce selective cell proliferation, resulting in

clonal expansion of aberrant cells lacking the function of genes critical for regulation of hematopoiesis. In addition, we applied a recently developed quantitative technique to detect and quantify DNA sequence loss from a region of mouse chromosome 2, which is altered in radiation-induced myeloid leukemia. This region of the genome is particularly useful for identifying candidate regulatory tumor suppressor genes whose functional loss may lead to leukemogenesis.

The specific aims were to determine whether radiation or benzene-induced leukemias in mice show recurrent loss of sequence from chromosome 2 of SJL mice, and to determine whether benzene or radiation induces preferential loss of sequence from mouse chromosome 2 in stem-cell populations, which results in a clonal advantage for the affected cells.

An original aim of the proposal was to determine whether radiation-induced loss of DNA sequence from chromosomes 11 and 13 in stem cells was an early event after radiation exposure of mice predisposed to radiation-induced leukemogenesis. Progeny from individual stem-cell clones were analyzed using quantitative polymerase chain reaction (PCR). There was no preferential loss of sequence (detection sensitivity of 10%) from this region of the genome, and thus we changed the primary genomic region of analysis from murine chromosome 11 and 13 to chromosome 2.

Accomplishments

Myeloid leukemias were generated in SJL mice by exposure to ionizing radiation (3.0 Gy).

Thirty percent of the irradiated mice developed leukemia. Preliminary analyses of the radiation leukemias using comparative genomic hybridization showed that chromosome 2 was lost at a higher frequency than chromosomes 11 or 13. In order to more narrowly define the region of genomic loss, we performed copy-number analysis of regions on chromosome 2 using DNA extracted from spleens of 27 mice. Five were unexposed controls, 11 were confirmed leukemic spleens, and 11 were from exposed mice without morphologic evidence of leukemia.

The method used for copy-number analysis was a newly developed fluorescence analysis technique developed using real-time PCR with regionally specific primer pairs. This quantitative PCR procedure is based on the Applied Biosystems' 5' exonuclease (TaqMan™) sequence detection system

and has several advantages over other techniques for determining regional DNA copy number. Unlike loss of heterozygosity (LOH), this method does not require heterozygosity at the markers being analyzed; therefore, all markers are informative. Furthermore, this method can differentiate between deletions and amplifications, which LOH cannot.

Figure 1 shows regions of chromosome 2 commonly lost in leukemias of SJL mice. The recurrent region of deletion, which is roughly defined by the overlap of the gray areas in the plot, encompasses approximately 10 cM. Analyses of additional leukemic specimens are underway using additional markers in the chromosome 2E region to narrow the region of common deletion. Additional, albeit preliminary, data suggest that a region showing homozygous deletion of two markers is present in some tumors. These data will facilitate searches for a candidate tumor-suppressor gene whose loss, induced by radiation, contributes to leukemogenesis. We continue to pursue narrowing the region of deletion on chromosome 2 to about 1 MB to allow generation of knockout mouse models to evaluate gene function. Data generated from the LDRD funding mechanism will provide opportunities to secure additional funds for pursuing identification of tumor-suppressor genes altered in radiation-induced leukemias.

Publications

D.G. Ginzinger, T.E. Godfrey, J. Nigro, D. Moore, M.G. Pallavicini, and R.H. Jensen, "Measurement of DNA Copy Number at Microsatellite Loci Using Quantitative Real Time PCR Analysis" (submitted to *Nature Genetics*).

MOUSE CHROMOSOME 2

		Sample Number						
cM	Marker	7 SJLs	11.4*	2.5*	12.2*	2.4B*	8.5**	2.1B**
2.2	D2Mit356	2	2.03 '	2.12	2.00	2.33	1.54	2.42
3.3	D2Mit175	2	1.90	2.05	1.84	2.52	1.46	1.71
25.1	D2Mit65	2	2.05	2.09	1.81	2.02	1.67	2.09
38.2	D2Mit9	2		2.45			1.73	1.99
50.3	D2Mit100	2					1.49	1.62
54.6	D2Mit63	2					1.48	1.97
	D2Mit62	2					1.52	1.94
	D2Mit395	2					1.94	2.21
56.8	D2Mit337	2		1.74	2.15		1.76	2.44
	D2Mit304	2		2.16	2.48		1.74	2.44
	D2Mit447	2		1.98	2.17		1.73	1.77
61.2	D2Mit224	2		1.69	2.18		1.76	2.91
73.2	D2Mit262	2		1.86	2.21		1.81	2.38
78.7	D2Mit142	2	1.95	2.00	2.30		1.74	2.18
85.2	D2Mit415	2	1.75	1.93	1.95		2.16	2.06
	D2Mit112	2	1.67	1.91	1.91		2.14	2.11
	D3Mit12	2	1.87	1.99	2.08	2.05	1.66	1.95
	D7Mit7	2	1.88	1.93	1.92	2.13	1.63	1.86
	D12Mit10	2	2.21	1.93	2.04	1.82	1.58	2.00

* = Leukemic
** = Non Leukemic

Figure 1. Regions (shaded) of chromosome 2 that are commonly lost in leukemias of SJL mice.

Environmental Genome Survey and Use of Microarray Technology

Principal Investigators: Tamas Torok and Stanley Goldman

Project No.: 96047

Project Description

This FY98 project is the continuation of a three-year project concerning the polyphasic characterization of selected microbial ecosystems in damaged environments. This characterization involves small-subunit ribosomal RNA (SSU rRNA) coding-gene sequencing and signature-lipid biomarker analysis. As a result of the LDRD-supported environmental genome survey, we have collected sufficient data and experience to advance the research to a higher level—by using microarray-based methods to accelerate the characterization of intrinsic microbial communities in the environment.

Microbial communities in nature are complex, highly integrated, dynamically changing, diverse assemblies of microbial populations. Characterization of these communities is of major importance for any *in situ* or *ex situ* bioremediation effort. Standard microbial-ecology procedures have in the past relied on

isolating and growing microorganisms, but conventional media and culturing techniques have resulted in identifying less than 1% of the vast diversity of microorganisms in nature. To better assess microorganisms occurring in nature, and (to a certain extent) to test the unique properties they possess that may act on pollutants at damaged sites, we have characterized microbial communities at the molecular and biochemical level and used this information to develop new methods of cultivation for subsequent rapid identification of the isolates.

Accomplishments

Last year, we worked with several dozen soil, sediment, and water samples from sites with different organic-matter content and various contaminants. We sought the direct characterization of microbial communities by extracting total genomic DNA from the samples while also isolating a large number of microorganisms capable of growing under laboratory conditions. Samples were taken from the highly contaminated San Juan Bay in Puerto Rico, the now-closed Alameda Naval Air Station, subsurface rock cores from the Test Area North (TAN) site in Idaho, acid mine drainage, a transmission oil spill in the Bay Area, and from ex situ bioreactors that remediate methyl ethyl ketone (MEK) and methyl tertiary butyl ether (MTBE), respectively.

To isolate large numbers of intrinsic microorganisms, isolation and culturing techniques simulated the natural environment where the sample originated. Soil and rock extract were prepared from either pristine or contaminated samples or from a standard commercially available potting soil and added to media. Low-nutrient media were used often with low agar or gellan gum content, providing a more colloidal growth environment. Additionally, selective isolation media for actinomycetes, heterotrophic bacteria, sulfur oxidizer, autotrophs, and fungi were chosen. Cultures were incubated in the dark at room temperature or below. After isolation and preliminary screening, we immediately preserved cultures to avoid potentially damaging further subculturing, and we maintained them at $-80°C$.

Prior to DNA extraction, microorganisms were grown and harvested by centrifugation. Several DNA extraction protocols were adapted. Polymerase chain reaction (PCR) amplification of small subunit rRNA genes was optimized. Primer sequences were derived from Escherichia coli for bacteria, and from Saccharomyces cerevisiae for eukaryotes. Following cycle sequencing with dye terminators, we performed automatic sequencing with an ABI PRISM 377 DNA Sequencer. We updated the sequencing data collection and base calling software and changed the sequencing chemistry to the more sensitive energy-transfer "Big Dyes." Edited SSU rRNA gene sequences were analyzed and aligned with the help of the Ribosomal Database Project and other on-line software protocols.

The manufacturer of the microbial identification system (MIDI) provided sample preparation protocol for fatty acid methylester analysis (FAME). Sherlock version 2.11 (MIDI) was used for peak naming, database comparison, strain identification, and two-dimensional plot and dendrogram analysis.

Procedures for sample preparation, microbial identification, and relationship analysis using a BIOLOG MicroLog 3 System followed manufacturers recommendations.

During the FY98 performance period, dozens of environmental samples were characterized and several hundred strains isolated and preserved. The molecular-level genotypic and phenotypic description of intrinsic microbial communities helped us better understand the samples, the activity of micro-organisms, and their fate and influence. This description also supported the optimization of two ex situ biostimulation technologies. Through collaboration with other projects, five student interns participated, learned, and used the new techniques. Important scientific topics could be resolved, such as the phylogenetic discrimination of close relatives in the non-proliferation project and characterizing rock-inhabiting and TCE-degrading microorganisms (or those growing on MEK and MTBE) as the sole carbon source.

The microarray approach would have enabled us to use small hybridization volumes, high-array densities, and fluorescence labeling and detection schemes. Because of circumstances beyond our control, this portion of the project could not be accomplished. High-density microarrays coupled with detailed biochemical and genetic analysis greatly speed up functional genomics in many areas of biology. It is of paramount importance that Berkeley Lab establishes this core capability for microbiologists, as well.

As a result of this successful project, the new project under the DOE's Initiatives for Proliferation Prevention and the Work for Others project with the FBI are largely structured around the hardware, capabilities, and expertise established under this project.

Materials Sciences Division

A New Strategy for the Introduction of Biocompatible Coatings onto Material Surfaces

Principal Investigator: Carolyn Bertozzi

Project No.: 97021

Project Description

There is an urgent need in the materials and biotechnology industries for new biocompatible materials. Many currently available materials, such as metals, ceramics, and organic polymers, have favorable bulk properties but are chemically incompatible with living tissue. The chemical composition of the material surface is very different from the bioenvironment, precluding the formation of an adhesive layer at the biological/material interface. This problem could be solved if the material surface were made to resemble the biological tissue more closely.

During the last two years, we have established a research program aimed at developing a revolutionary new technology for coating materials with a biocompatible surface that mimics the bioenvironment. Our strategy for controlling material surface biocompatibility is to coat the material with a new surface that perfectly mimics the bioenvironment. The unique feature of our approach is that we use living cells to construct the biomimetic coating. The challenge is to develop a method for attaching a uniform layer of cells to a material surface in a chemically defined fashion without damaging the cells' physiology. We have developed two new technologies to meet this challenge. First, we coat material substrates with a monolayer of reactive organic functional groups using the technique of organic self-assembly. Second, we decorate cells with a complementary reactive functional group via biosynthetic engineering of cell-surface oligosaccharides. The two functional groups are designed to be mutually reactive under physiological conditions and will covalently ligate to form a uniform layer of cells on the material surface. Once

the material is coated with cells, its surface will mimic the bioenvironment. This breakthrough technology has the potential to expand the utility of metals, polymers, and ceramics in biotechnology and medicine.

Accomplishments

There are two critical technical elements in this novel material-coating strategy: (1) the metabolic incorporation of chemically reactive functional groups onto cell surfaces and (2) the introduction of organic monolayers with complementary reactivity onto materials. The first of these technologies was established during the first year of the LDRD Program and is summarized as follows.

We developed a powerful new method for installing an unnatural reactive functional group, the ketone, onto cell surfaces by simply feeding the cells a synthetic sugar molecule. The cells ingest the synthetic sugar and convert it to a cell surface-bound oligosaccharide, delivering ketone groups to the cell surface. The choice of the ketone as a reactive group was based on two important considerations. First, the ketone is chemically unique among the functional groups normally present on a cell surface. Second, the ketone can be selectively coupled with hydrazide groups under biologically compatible conditions, affording the corresponding hydrazones. This enables the selective attachment of ketone-coated cells to hydrazide-coated material surfaces, and the concomitant formation of a biocompatible coating on the material, as depicted in Figure 1.

Our major accomplishments during the last year focused on the development of new methods for material surface coating, the second objective outlined above. The goal was to establish a general method for attaching a biocompatible monolayer functionalized with hydrazide groups onto metals and ceramics. An essential feature of the surface coating was that it be well hydrated and resist nonspecific protein adsorption. To accomplish this goal, we developed a method for the polymerization of 2-hydroxyethylmethacrylate (HEMA) on surfaces, starting from a siloxane methacrylate base installed on the material surface through covalent self-assembly. The procedure is depicted in Figure 2.
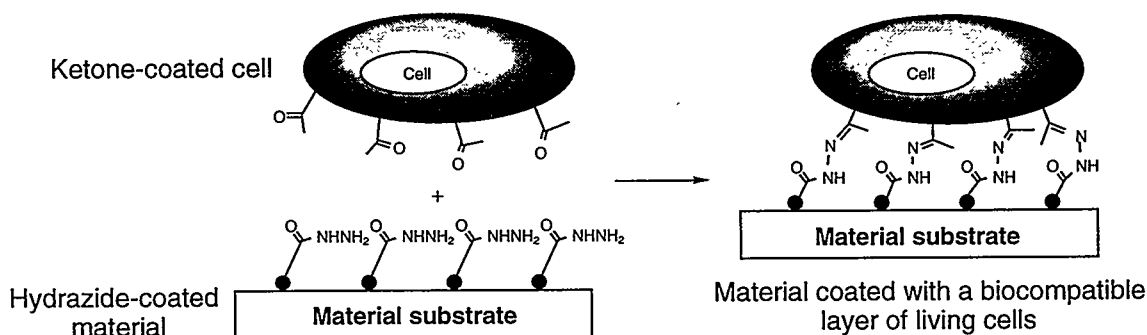
Figure 1. Introduction of a biocompatible coating of cells onto a material surface. The material is first modified with an organic monolayer containing a hydrazide group. A layer of cells metabolically decorated with complementary ketone groups is then covalently attached to the surface. The new surface resembles biological tissue and is fully biocompatible.

We initially demonstrated the method on mica surfaces because these have sufficient flatness for analysis by atomic force microscopy (AFM). We were able to analyze the hydration of the HEMA coating and protein adsorption from solution in real time by AFM. These studies have provided insight into the surface requirements for viable cell attachment. The method is now being extended to surface coating of ceramic materials and titanium alloys. In addition, methods for the incorporation of hydrazide groups into the HEMA copolymers are being explored.

Publications

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K.J. Yarema and C.R. Bertozzi, "Chemical Approaches to Glycobiology and Emerging Carbohydrate-Based Therapeutic Agents," Curr. Opin. Chem. Biol. 2, 49–61 (1998).

K.J. Yarema, L.K. Mahal, R. Bruehl, E.C. Rodriguez, and C.R. Bertozzi, "Metabolic Delivery of Ketone Groups to Sialic Acid Residues: Application to Cell Surface Glycoform Engineering," J. Biol. Chem. 273, 31168–31179 (1998).

J.L. Lee, T.J. Baker, L.K. Mahal, J. Zabner, C.R. Bertozzi, D.F. Wiemer, and M.J. Welsh, "Engineering Novel Cell Surface Receptors for Virus-Mediated Gene Transfer," Proc. Natl. Acad. Sci. USA (submitted).
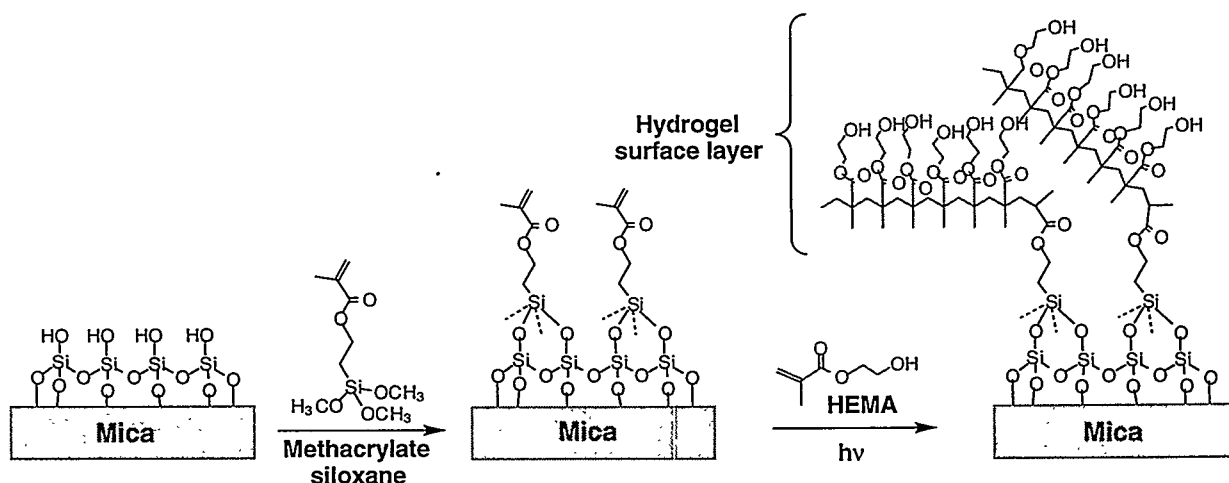
Figure 2. A method for the synthesis of polyHEMA films on mica.

Time-Resolved Spectroscopy of Strongly Correlated Materials

Principal Investigator: Daniel Chemla

Project No.: 97022

Figure 1. Pump-probe spectrum at 76 ps (heavy solid line), shown with incident laser spectrum (light solid) and absorption spectrum (dashed).

Project Description

The objective of this research has been to study the nonlinear optical response of magnetic insulators and related materials, using femtosecond (fs) pulsed laser spectroscopy. Previously, researchers have successfully used pulsed laser techniques to clarify the physics of charge dynamics and Coulomb correlation in semiconductors as well as quasiparticle-lattice relaxation in metals. The application of these tools to the charge and spin dynamics of strongly correlated electron systems is now appropriate and compelling. This research is highly relevant to our understanding of high-temperature superconductors, which are magnetic insulators in their undoped state.

During the course of this project, we have investigated the linear and nonlinear optical properties of several strongly correlated electron materials, both insulating and metallic. We have also developed a variety of spectroscopic tools, previously unavailable in our laboratory, to enhance our experimental capabilities. The emphasis throughout has been to identify and develop areas in which time-resolved spectroscopy may be utilized to provide new information about magnetic and other electronic correlation phenomena.

Accomplishments

We have applied time-resolved nonlinear optical spectroscopy to probe magnetic dynamics in one well-studied strongly correlated insulator, Cr_2O_3, and we have observed a novel nonlinear optical effect associated with the occupation dependence of the magnon dispersion relation. The existence of this effect presents the opportunity to use pulsed lasers to manipulate and study magnetic excitations in this and other strongly correlated insulators. Figure 1 shows the spectrally resolved nonlinear signal, which we observe in pump-probe spectroscopy of the exciton-magnon transition. At excitation densities of $\sim10^{-3}$/Cr, the data are well described in terms of two components: (1) a prompt, spectrally featureless
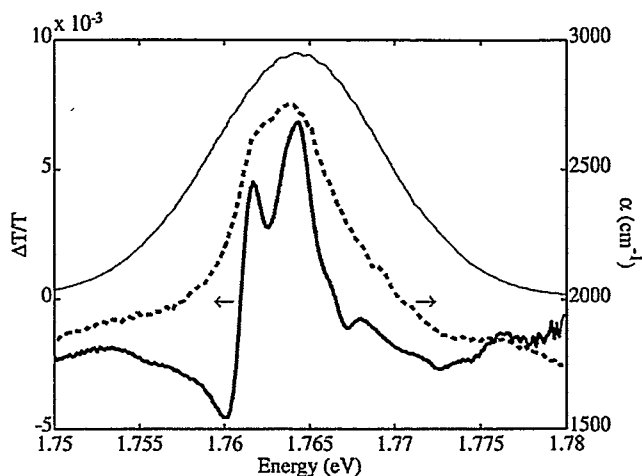
photoinduced absorption (PIA), which decays on time scales longer than 100 ps, and (2) the complex spectral feature shown in Figure 1, which grows in strength over tens of picoseconds and starts to decay after ~1 ns. The magnitude and qualitative lineshape shown in Figure 1 may be explained by recognizing that each optical excitation creates a magnon excitation and that the interaction of these excitations renormalizes the overall magnon band structure. The exciton-magnon lineshape, which derives from a weighted sum of excitons and magnons at k and –k, reflects this renormalization and produces the derivative-like pump-probe signal that we observe.

The time evolution of this magnetically induced nonlinear optical effect is shown in Figure 2, which shows the response at different wavelengths, keeping the center wavelength of the laser fixed. These time traces clearly show the two different contributions to the nonlinear optical signal—with frequencies well outside the exciton-magnon line exhibiting only prompt PIA, and frequencies inside the line exhibiting picosecond dynamics. The time scale for these dynamics is not currently understood, but we hypothesize that it is associated with magnon diffusion. Having established that this effect exists and can serve as a time-resolved probe of spin relaxation, we are currently investigating the influence of above-gap excitation on the exciton-magnon line to clarify the coupling between the correlation-induced gap and magnetic excitations.

We have also studied the nonlinear optical properties of the correlation gap in $Sr_2CuO_2Cl_2$, which is a model system for the parent compounds of cuprate
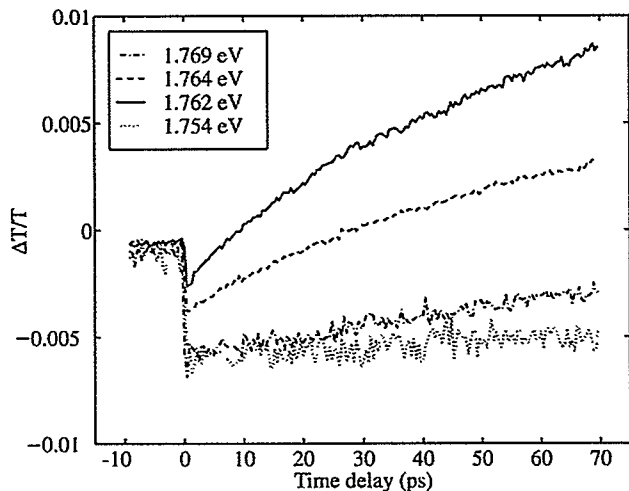
Figure 2. Time-resolved pump-probe signal at different energies.

superconductors. At energies well above the gap, we observe a strong photoinduced absorption in contrast to the usual bleaching observed in conventional band semiconductors. The initial decay of this absorption occurs on picosecond time scales before rolling over to qualitatively different dynamics with a time scale of tens of nanoseconds. Both the sign of this signal and its dynamics involve exciting and unexplored physics, and we are working with L. Sham of UC San Diego to understand these results.

In collaboration with J. Orenstein, we have also used time-domain terahertz spectroscopy to measure the quasiparticle scattering rate renormalization in the strongly correlated itinerant ferromagnet $SrRuO_3$. In these experiments, we observe strong quasiparticle renormalization, which sets in below the ferromagnetic transition temperature of the material (150 K). This renormalization has been observed in heavy fermion compounds, where it is understood as the development of coherence between heavy f-electrons and lighter d-electrons. We believe that ours is the first observation of such an effect in a compound with only p-d hybridized bands crossing the Fermi level.

Publications

J.S. Dodge, A.B. Schumacher, J.-Y. Bigot, D.S. Chemla, N. Ingle, and M.R. Beasley, "Time-Resolved Observation of Magnon Renormalization Effects in Cr_2O_3" (submitted to *QELS '99 Technical Digest*).

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J.S. Dodge, A.B. Schumacher, J.-Y. Bigot, D.S. Chemla, N. Ingle, and M.R. Beasley, "Optically Induced Nonequilibrium Magnon Population and Renormalization in Cr_2O_3" (in preparation).

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Electron and Spin Dynamics in Metallic Materials

Principal Investigator: Daniel Chemla

Project No.: 98020

Project Description

The aim of this project is to study the dynamical response of the electrons and spins in metallic materials excited with ultrashort laser pulses. This is a challenging new area of physics that has received much impetus from recent experiments in transition metals. The study will focus on the correlation effects associated with the elementary interactions between the electrons, their spins, and the lattice modes (Coulomb and exchange interactions, spin-orbit coupling, and electron-phonon and spin-phonon interactions). The general motivation of this research is to bring new insights into the mechanisms that are at the origin of the physical properties of metals such as ferromagnetism, superconductivity, magnetoresistivity, and super-paramagnetism. The project also has initiated a collaboration between the Institut de Physique et Chimie des Materiaux (ICPM) de Strasbourg, France, and the LBNL Materials Sciences Division.

Through this collaboration, LBNL and ICPM will address several questions raised when magnetic materials are excited in the femtosecond regime, including: (1) what is the correlation length over

which the spin reversal takes place; (2) what is the fastest demagnetization rate that can be obtained when the metal makes a ferro- to paramagnetic phase transformation; (3) what is the influence of nonthermalized electronic populations on the spin dynamics; (4) how is the total momentum conserved during spin flip processes; (5) is the concept of magnetic specific capacities still valid in time scales of a few tens of femtoseconds; (6) if the electron and spin populations are not in equilibrium during a short time, how should the concept of different electronic and spin temperatures be understood; (7) what is the role of spin-orbit coupling in the demagnetization process?

Accomplishments

J.-Y. Bigot from ICPM spent two months at LBNL experimenting with an ultrafast pump/probe technique on a series of samples fabricated at the ICPM. These preliminary experiments were aimed at identifying the optimal parameters for future, more thorough investigations. The materials investigated included (1) nanometer-thick copper, silver, and gold films; and (2) nanocrystals with a diameter in the 5- to 10-nm range that are of the same materials embedded in glass matrices.

The experiments have identified the localized plasmon resonance in nanocrystals as the most interesting system to investigate. The plasmon resonance corresponds to collective oscillations of the electronic gas that can couple to the electromagnetic field because of the restricted geometry. The dynamics of the electronic excitations of these plasmon resonances that are coupled to one-photon transitions have been investigated by several groups, in particular by J.-Y. Bigot's group at ICPM. However, the up-to-date dynamics of the excitations coupled to two-photon transitions have been neither studied nor observed. In the case of silver nanocrystals, the accessible one-photon plasmon resonance appears in the absorption spectrum as a broad peak centered at $h\nu_{R-1ph} \approx 3$ eV. It is expected that the two-photon states would correspond to a similar transition energy and thus to photons in the range $h\nu_{R-2ph} \approx 1.5$ eV, which perfectly matches the energy of the 15-fs Ti:sapphire laser available in D. Chemla's laboratory at LBNL.

During a visit to ICPM by D. Chemla in October 1998, results of the preliminary experiments were discussed with the ICPM staff. An optimized silver nanocrystal sample with $h\nu_{R-2ph} = 1.47$ eV was prepared at the ICPM and brought back to LBNL. Currently, an experimental setup for performing regular and interferometric pump/probe experiments on the sample is being developed at LBNL.

Development of Atomic-Resolution X-Ray Fluorescence Holography for Materials Analysis

Principal Investigators: Charles Fadley, Thomas Earnest, Zahid Hussain, Rupert Perera, Abraham Szöke, and Stephen Cramer

Project No.: 98021

Project Description

This project will develop x-ray fluorescence holography at the Advanced Light Source (ALS) as a novel probe of atomic structure with sub-Angstrom resolution. This newly discovered technique has been shown in prior experiments to be capable of providing local atomic-structure information around a given elemental constituent of a material without the need for macroscopic single-crystal samples. This method developed from the initial suggestion by Szöke (in 1986) of using localized atomic emission events as sources of outgoing reference waves for holography. It was first realized experimentally with photoelectrons in 1990, then achieved with fluorescent x-rays in 1996, and finally achieved with gamma rays via the Mössbauer effect in late 1997.

Our focus is on x-ray fluorescence holography (XFH), in which the diffraction modulations of x-ray intensity are only of order $\sim\pm0.1\%$, but for which the holographic images are expected to be much more accurate than those obtained with the more strongly scattering photoelectrons. X-rays also provide a probe that can reach into the bulk of a sample, expanding the areas of application from surface science to materials science and ultimately the biosciences. In the simplest form of XFH, the modulations of a given single fluorescent energy are measured over a large solid angle above a sample surface, and then a Fourier-transform-like operation is performed on these measurements to directly yield atomic images in three dimensions. Prior work in other laboratories has applied this method to inorganic solids (Sr in $SrTiO_3$, Cu and Au in Cu_3Au) and a semiconductor dopant (Zn in 0.02 wt.% doped GaAs).

Beyond this approach, the Fadley group has been involved (in collaboration with Materlik et al.) in developing a more powerful form of XFH called multi-energy x-ray holography (MEXH), in which the incident radiation beam is used as the reference wave, and the outgoing fluorescence is used only to measure the wave field strength at a given emitting atom type. In this way, holograms at 5–10 incident energies can in principle be measured, with the analogous Fourier-like inversion providing more accurate atomic images (i.e., free of twin images and less affected by image aberrations). This type of measurement has so far been applied to hematite (Fe_2O_3) but is ideally suited for further exploitation at third-generation synchrotron radiation sources such as the ALS. This project will carry out multiple-energy x-ray holography experiments at the ALS in order to demonstrate the full potential of this exciting, new probe of atomic structure and prepare the groundwork for establishment of a proper facility for routinely carrying out such measurements. The first of these experiments will be proof of principle in nature, with more concrete applications to more complex systems at the end of the study (which will be continued under LDRD funding in FY99). The project makes use of several unique resources at LBNL:

- ALS Beamline 9.3.1, which yields high-brightness x-rays up to ~7.0 keV in energy (or down to 1.8 Å in wavelength) and with total usable fluxes at the sample of ~4×10^{10} s^{-1}.

- Multi-element semiconductor detectors consisting of approximately 12–30 working elements over areas of 2"–3" radius, each element counting with ~200 eV resolution at a rate of ~50 kHz (to be loaned by the Cramer group for this project).

- A high-accuracy sample goniometer capable of rotating samples over a large solid angle in measuring holograms, to be assembled specifically for this project.

The first samples to be studied in the next phase of the project will include:

- MnO: this material will aid in determining both the heavy atom (Mn) positions and the light atom (O) positions in a mixed-composition substance.

- Ge doping in Si: this will further aid in determining short-range structure around a dopant, first for the test system of a single

atomic layer of Ge sandwiched between thick Si layers. The dopant level will be reduced from the levels studied previously in Zn/GaAs in order to determine the lower threshold for such MEXH studies.

- Mosaic crystal of a biologically interesting molecule: this sample (probably a bacterial hydrogenase containing metal atoms surrounded by sulfur) will be chosen once the first two test cases are completed, in collaboration with S. Cramer and T. Earnest, and will contain a transition metal atom in a unique site around which the structure will be determined.

- $La_xSr_{1-x}MnO_3$: this material is one of the colossal-magnetoresistive oxides, and it will be studied to determine whether holographic imaging of the O atoms around Mn can detect the small Jahn-Teller distortions that occur as the material changes from ferromagnetic metal to paramagnetic insulator.

Accomplishments

During the past year, the mirrors on Beamline 9.3.1 have been replaced, thus extending the energy range to higher values and increasing the flux available for these experiments by about one order of magnitude. Perera and Fadley are both members of the team involved with this beamline, and thus sufficient beamtime will be available in the continuation of this study. The 30-element x-ray detector has also been successfully used for the first time by the Cramer group in other experiments, and a smaller 12-element detector that can be used in this work has also been made available to us. The sample goniometer (mostly available through the Hussain and Fadley group) is based on previous designs for photoelectron holography. Other details of the goniometer and experimental chamber design and construction are presently being worked out. During this period, theoretical calculations continuing earlier work have also been performed for optimizing the experimental data obtained in our coming multi-energy holography experiments.

Publications

C.S. Fadley and A. Szöke, "Atomic-Resolution Holography with Electrons, X-rays, and Gamma Rays," invited article for *Physics Today* (in preparation).

UV Optical Studies of Wide Bandgap Semiconductors at ALS

Principal Investigators: Wei Shan, Joel Ager, Wladek Walukiewicz, Eugene Haller, and Howard Padmore

Project No.: 98022

Project Description

This project encompassed the construction and testing of a new endstation on the Advanced Light Source (ALS) Beamline 1.4 to perform spectroscopy in the ultraviolet (UV) area of the spectrum. By exploiting the high brightness and directionality of the bend magnet radiation, it is possible to make an intense, versatile source for spectroscopic studies in the 180–350 nm range. The source characteristics were measured and initial spectroscopic experiments were performed with semiconducting films of the III-V nitride family: InN (E_g = 1.9 eV), GaN (E_g = 3.4 eV), AlN (E_g = 6.1 eV), and their alloys. We chose this materials system because of the intense scientific interest in it due to the recent commercialization of high-efficiency blue and green light emitting diodes and the demonstration of blue cw laser operation.

Accomplishments

Beamline Construction and Source Characterization

A new experimental hutch was constructed (Beamline 1.4.1), and the requisite laser table and optics were installed. The source strength at the laser table (in the 240–800 nm range) was in good agreement with bend magnet calculations provided by the ALS Systems group. The total cw power at 350 mA ring current is 50-mW broadband at the UHV exit window. After beam shaping and diversion, the power is still 20 mW at the laser table. The capability of focusing the beam without intensity loss to a 100-μm and smaller spot sizes will be useful for studies with small samples.

Pressure Dependence of AlGaN Bandgap

The pressure dependence of the bandgap for a series of $Al_xGa_{1-x}N$ epitaxial films was measured. The bandgap was determined by optical absorption; pressure was applied with a diamond anvil cell (DAC). This experiment is difficult to perform with conventional UV sources because of the small size of

the samples (approximately 200 μm in diameter). The superior collimation of the ALS source, however, enabled the UV beam to be focused precisely on the sample in the cell. A spectrometer and charge-coupled-device camera were used to obtain the absorption spectra shown in Figure 1. The pressure dependence of the bandgap for these alloys (Figure 2)
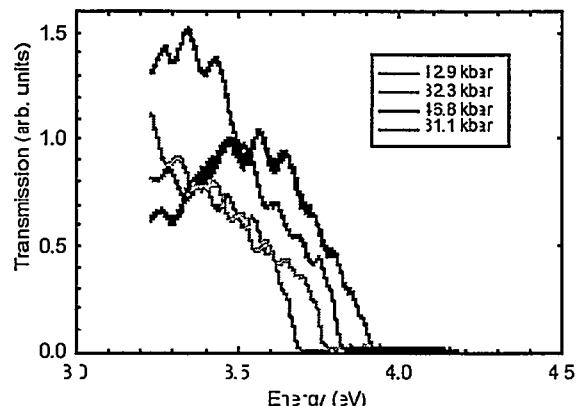
Figure 1. Absorption spectra of AlGaN epitaxial film obtained as a function of pressure in diamond anvil cell. Focused UV light from ALS Beamline 1.4.1 was used as the UV light source.
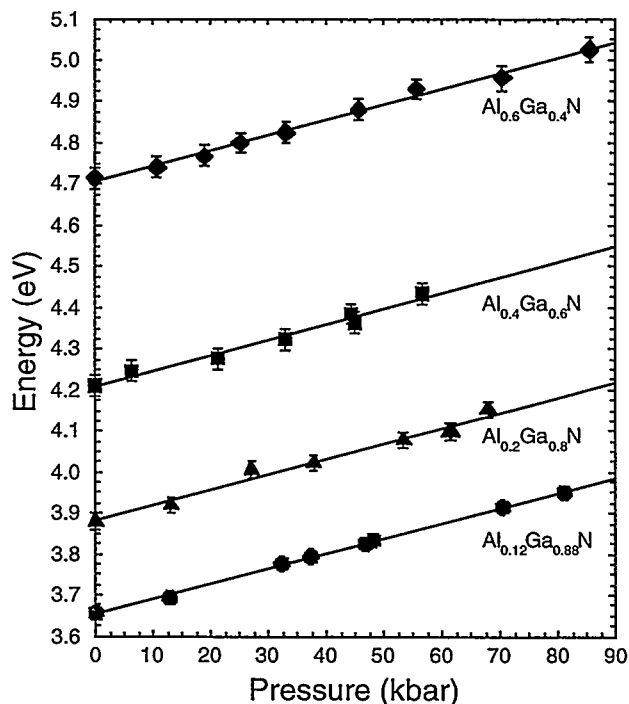
Figure 2. Pressure dependence of the fundamental gap of AlGaN samples obtained from UV absorption measurements at ALS.

is being used to understand the band structure of III-V nitrides.

Photoluminescence in InGaN Quantum Wells

Photoluminescence (PL) measurements were performed in InGaN quantum wells at 77 K. A 0.25-m monochromator was used to select the excitation wavelength, which was varied from 300 nm (4.13 eV) to 350 nm (3.54 eV). The results are shown in Figure 3. Very little PL was observed for excitation energies below 3.5 eV, the bandgap of GaN. This demonstrates that the PL from the InGaN quantum wells originates from electrons diffusing from the GaN cladding layer to the well rather than from direct excitation of carriers in the quantum well. This experiment demonstrates that Beamline 1.4.1 can generate sufficiently bright, tunable UV light for investigation of IIIV-V semiconductors.
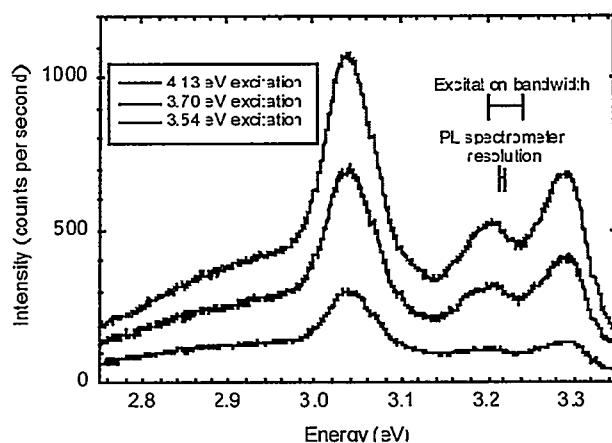
Figure 3. Photoluminescence spectra of $In_{0.15}Ga_{0.85}N$ quantum wells excited by UV light from ALS Beamline 1.4.3. The peak at 3.05 eV is from the quantum well. Peaks at 3.28 and 3.21 eV are donor-acceptor pair recombination and LO phonon replica in GaN, respectively. PL intensity decreases with excitation wavelength due to reduced absorption depth in 200-nm GaN cladding layer.

Publications

J.W. Ager III, W. Shan, K.M. Yu, W. Walukiewicz, E.E. Haller, M.C. Martin, W. McKinney, and W. Yang, "Pressure Dependence of the Fundamental Energy Band Gap of AlGaN Alloys" (abstract submitted to March 1999 American Physical Society meeting; manuscript in preparation).

Phosphorescent Molecule as a Probe in Near-Field Optical Microscopy and Spectroscopy, and Electronic Correlation Effects on Transport Properties of Carbon Nanotubes

Principal Investigator: Dung-Hai Lee

Project No.: 97036

Project Description

This project addresses two theoretical problems. The first problem involves the use of a phosphorescent molecule as a probe in near-field optical microscopy and spectroscopy. In an interesting experiment, E. Burstein and I.A. Yurchenko showed that when a layer of C_{60} molecules is forced to make contact with a metallic substrate, an otherwise dark phosphorescence (i.e., triplet $\rightarrow$ singlet emission) line is turned on. This observation has considerable theoretical interest.

The second problem involves electronic correlation effects on the transport properties of carbon nanotubes.

Accomplishments

There were three specific accomplishments in this project:

- We explained the substrate-induced phosphorescence of C_{60}. We found that substrate-induced phosphorescence of C_{60} can be used as the guiding principle in building a tool for the near-field optical microscopy and spectroscopy.

- We showed that the magnetic environment has an important effect on the presence or absence of superconductivity in the charge stripe of $La_{1.6-x}Nd_{.04}Sr_xCuO_4$.

- We demonstrated that electronic correlation in (n,n) carbon nanotubes can cause super-conductivity on doping.

In studying the phosphorescent molecule as a probe, we realized that the quantum mixing between C_{60} and the substrate relieves the spin selection rule for the molecule. Moreover, we found that the induced

phosphorescent intensity is proportional to the local-spin spectral function of the substrate (i.e., $I(\omega) \propto Im[\chi(\Delta - \omega)]$, where Δ is the singlet-triplet energy splitting). This result is very important because it suggests that we can use the C_{60} phosphorescence as a local probe of the spin density of states, just as scanning-tunneling microscopy can be used to probe the single-particle density of states.

We also studied correlation effects in the (n,n) carbon nanotubes, using the perturbative renormalization group method. We found that, on doping, the electron-electron interaction strongly enhances the superconducting fluctuation. This result suggests that the doped nanotubes can be superconductors at low temperatures.

Publications

Y. Krotov, D-H. Lee, and S.G. Louie, "Low Energy Properties of the (n,n) Carbon Nanotubes," *Phys. Rev. Lett.* 78, 4245 (1997).

Y. Krotov, D-H. Lee, and A. Balatsky, "Superconductivity in Metallic Stripes," *Phys. Rev. B* 56, 8367 (1997).

Y. Krotov and D-H. Lee, "Induced Molecular Phosphorescence as a Local Probe of Spin Spectral Function" (preprint).

Determining Macroscopic Materials Properties from Microscopic Calculations

Principal Investigators: Andrew Canning, Daryl Chrzan, Marvin Cohen, Steven Louie, and John Morris, Jr.

Project No.: 96041

Project Description

The goal of this research is to construct new predictive models of the properties of real materials by exploiting advances in computer hardware and computational techniques, advances in the

fundamental theory of bonding in solids, and advances in the theory of plastic deformation.

The project is a collaborative program to compute the macroscopic properties of materials by combining modern *ab initio* methods in theoretical solid state physics and materials science and by exploiting the advanced computational facilities at LBNL. The *ab initio* component involves electronic structure calculations similar to those that the investigators performed in the past, but rephrased to exploit new computational methods that take advantage of parallel processing. Using only the atomic numbers and masses of constituent atoms, we can now compute electronic, vibrational, structural, and thermodynamic properties of, and dynamic processes in, materials. These fundamental calculations are used to develop scaling formulas to determine the macroscopic properties of complex materials and define input parameters for property simulations. Systems under investigation include fullerene base solids, semiconductor clusters, and hard materials.

Accomplishments

Clusters and Nanocrystals

Our activities in this area consist of theoretical studies of small fullerenes, Si clusters, and semiconductor nanocrystals, with the goal of explaining and predicting the properties of these nanoscale systems.

We have investigated the electronic and structural properties of several isomers of molecular C_{36} using the pseudopotential-density functional approach. These calculations show that substitutional doping with nitrogen can lead to a 10% decrease in the C-C bond lengths of C_{36}, the effect of which is explained using a simple mechanism. Furthermore, we have calculated endohedral binding energies and demonstrated that C_{36} is perhaps the smallest fullerene size that can easily trap a range of atoms. The nuclear-magnetic-resonance chemical shifts, evaluated for the two lowest energy fullerene isomers, show that they are sufficiently different chemically to be distinguishable experimentally. Among the experimentally observed structures of molecular C_{36}, our calculations show that the structure with D_{6h} symmetry is the most energetically favorable. Based on these results and the fact that D_{6h} is conducive to forming a periodic system, we propose a new solid phase of carbon on the basis of C_{36} fullerenes. Full structural relaxations and electronic density of states are evaluated using an *ab initio* pseudopotential planewave method within

the local density approximation. The calculated electron-phonon interaction potential is found to be substantially enhanced compared to C_{60}, indicating the possibility of larger superconducting transition temperatures than in alkali-doped C_{60} solids.

For semiconductor nanocrystals studies, we refined our Wannier function method for computing nanocrystal electronic structure. The refined method has been applied to compute electronic eigenenergies and to visualize electronic eigenstates for small-bandgap InAs nanocrystals. The agreement of our computational results with experiment elucidated some key aspects of quantum confinement. With this insight, we were able to develop an analytical Green's-function formalism for confinement physics.

A complementary effort to the Wannier function approach is our *ab initio* study of the optical transitions in Si quantum dots. Until recently, the modification of the gap from quantum confinement has not been examined using *ab initio* methods owing to the large size of the dots. The smallest dots measured contain on the order of 500 atoms. Using a new real-space formalism, we have carried out to realistic dimensions an *ab initio* investigation of the optical gap for the Si quantum dots as a function of cluster size. We considered clusters up to 30 Å in diameter, which contain over 1,000 atoms. The optical gaps are computed by adding the electron-hole Coulomb energy to the quasiparticle gap. Excellent agreement with measured values have been obtained.

Hard Materials

Our program of *ab initio* pseudopotential calculations of metals, carbides, and nitrides has led us to consider the hardness properties of exotic elemental solids, like seaborgium and hassium (elements 106 and 108). By studying our computational results for Ti, TiC, TiN, V, VC, VN, Cr, CrC, CrN, Mo, MoC, MoN, W, WC, WN, Re, ReC, ReN, Os, OsC, and OsN, we were led to the hypothesis that seaborgium and hassium might have very large bulk moduli. Preliminary LDA calculations seem to confirm this hypothesis.

Because shorter bond lengths are generally associated with harder materials, we have conducted a study of a new highly symmetric crystal made exclusively of sp2 bonded atoms. We performed calculations of the structural and electronic properties within the pseudopotential-density functional approach for two different compositions made of (1) pure carbon and (2) a carbon and nitrogen compound. In both solids, one of the carbon-carbon bond lengths is found to be 1.35 Å, which is considerably smaller than any carbon-carbon bond length found in other carbon solids. The bulk moduli are calculated to be 241 and 286 GPa for the pure carbon and the carbon-nitride compounds, respectively. We demonstrated that the relatively low bulk moduli (considering the short bond lengths found in the structure) result from the disruption of the carbon p bonding states. This result is probably unavoidable when trying to form a three-dimensional structure out of a planar configuration like the sp2 bonds. The calculated density of states and band structures show that the pure carbon form is metallic, whereas the carbon-nitride compound is a semiconductor. When carbon atoms are added to the interstitial regions, the carbon solid becomes insulating, and the bulk modulus increases to ~282 GPa.

We have also begun a study of structural relaxations in the presence of applied shear stresses. Initial calculations for titanium show that relaxations normal to the slip plane and the slip direction dramatically lower the stresses required for large shears. Simple models of the shear-energy barrier assume a sinusoidal relationship between elastic energy and the applied shear strain. Allowing electronic relaxation reduces the critical stress for $\{111\}\langle112\rangle$ slip by a factor of two over the sinusoidal approximation. Allowing structural relaxation reduces this stress by an additional factor of five.

Dislocation Dynamics

We have constructed kinetic Monte Carlo simulations of dislocation dynamics for dislocations confined to a finite-sized slip plane. These simulations reveal that dislocations in BCC materials may "roughen" and that the scaling properties of the roughened dislocations are consistent with those predicted by the Kardar-Parisi-Zhang equation. The simulations also reveal a length dependence to the average velocity that stems from the interplay between the generation of kinks at the surface and the generation of double-kink pairs in the bulk. Hence, the presence of grain boundaries and free surfaces may alter the average velocity of the dislocations.

We have also begun to explore the atomic-scale properties of dislocation cores in diamond. We have applied *ab initio* techniques to study the dislocation cores (in collaboration with X. Blase, Lyon). These calculations suggest that under a broad range of stresses, the core of the 90° partial in diamond cubic C is period doubled reconstructed.

Publications

X. Blase, D.C. Chrzan, A. Canning, and S.G. Louie, "Structure of Dislocation Cores in Diamond-Cubic Carbon" (in preparation).

J.R. Chelikowsky, S. Ogut, and S.G. Louie, "Optical Gaps and Screening in Quantum Dots," Proceedings of 9th International Conference on Modern Materials and Technologies, Florence, Italy (in press, 1998).

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A. Mizel and M.L. Cohen, "Electronic Transitions in InAs Nanocrystals Using Wannier Function Method," Solid State Comm. 104, 401 (1997).

S. Ogut, J.R. Chelikowsky, and S.G. Louie, "Quantum Confinement and Optical Gaps in Si Nanocrystals," Phys. Rev. Lett. 79, 1770 (1997).

Electromigration in Nanometallic Junctions

Principal Investigator: Paul McEuen

Project No.: 98040

Project Description

Metals carry large electrical currents in applications ranging from microelectronics to power transmission. One of the issues that arises in these applications is that the current flow can result in the movement and rearrangement of atoms within the metal. Such electromigration leads to conducting properties that change as a function of time. In general, this is a problem; electromigration is a major failure mode for many electronic devices. In this project, however, we use electromigration to create useful structures, namely, nanometer-scale gaps between two metallic electrodes. Such gaps are useful for making electrical connections to nanometer-scale objects such as conducting molecules and nanocrystals. Currently, no reproducible, reliable technique exists for the creation of such gaps.

To make these structures, electron-beam lithography is used to pattern a free-standing resist bridge. Two shadow evaporation steps are then used to create an overlap of two thin Au metallic layers. These metallic junctions are 100 nm across and 10 nm high and have a resistance between 10-100 Øhms. A Field Emission Scanning Electron Microscopy (FESEM) image and I-V curve of the junction is shown in Figure 1 (before). A voltage of approximately 0.5 volts is then applied across the junction, and the resistance of the structure begins to evolve in time. After an initial period of slow change, typically a large change occurs in which the resistance of the junction suddenly increases. After the junction "breaks," its resistance is typically

greater than 100 kW and is hence dominated by tunneling between the two electrodes. A FESEM image and I-V curve of a junction after breaking are shown in Figure 1 (after). A small gap (of a few nanometers) is seen between the two electrodes after breaking.

Accomplishments

Using this technique, we can now routinely and reliably produce electrodes with nanometer-scale separations. We have fabricated literally hundreds of these junctions. Using previous techniques, it was difficult to produce more than a few at a time. This improvement in the reliability and ease of electrode patterning will be a tremendous boost to the field of molecular electronics. The difficulty in creating electrical connections at the nanometer size scale has been a major impediment to progress in the field, and this work is an important step toward solving that problem.

Publications

H.K. Park, A. Lim, A.P. Alivisatos, and P.L. McEuen, "Controlled Electromigration for Producing Nanometer-Scale Electrodes" (in preparation).
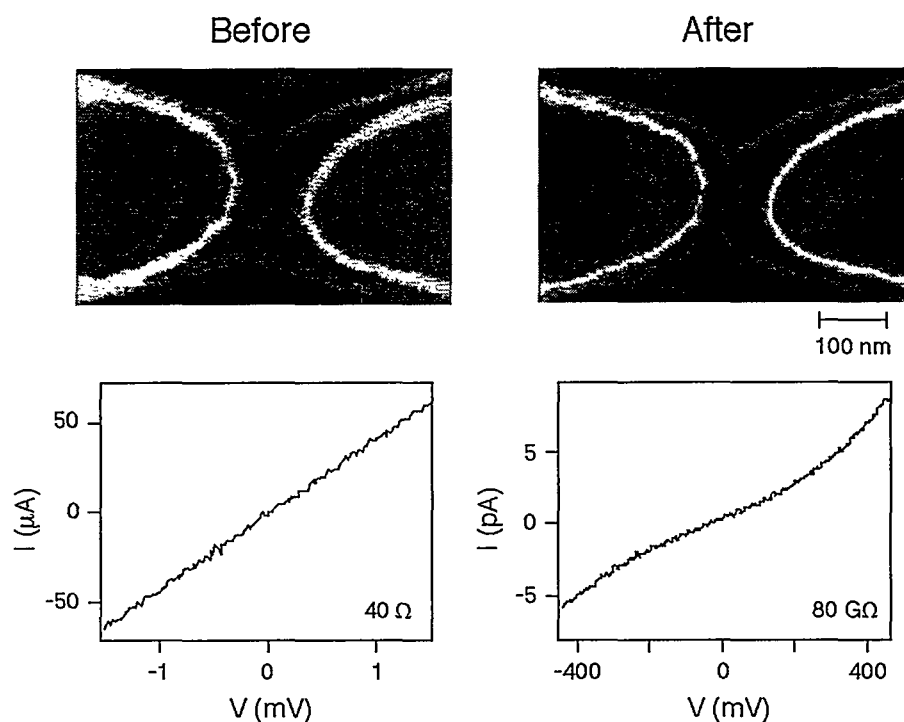
Figure 1. FESEM micrographs and I-V characteristics of an Au overlap junction before and after the application of a large voltage bias that breaks the junction.

Investigation of Quantum Well States in Magnetic Nanostructures

Principal Investigator: Zi Qiu

Project No.: 98041

Project Description

The formation of quantum well (QW) states in magnetic nanostructures results in many fascinating properties such as oscillatory magnetic coupling and giant magnetoresistance (GMR). This project investigated the fundamental behaviors of QW states using photoemission techniques at the Advanced Light Source (ALS). In particular, we investigated the evolution of QW states in the energy-thickness plane.

Because of the short wavelength of electrons in metals, film thickness must be controlled on the atomic scale. To conduct a systematic study, we performed photoemission on wedged samples, which provide a continuous change of film thickness. Wedged samples, however, require a local probe, which is not common in photoemission. ALS Beamline 7.0.1.2's capability of creating a fine photon beam size (~50 to 100 mm) with high brightness (>10^{12} photons/sec at resolution power of 10,000) allowed us to perform a photoemission experiment on a wedged sample.

Accomplishments

We succeeded in performing our photoemission experiment on wedged Cu film grown on fcc Co(100). The minority spin band of the Co electrons served as a potential well to confine the Cu electrons into QW states, which appeared as peaks in the photoemission spectra. Figure 1 shows the result on the Cu wedge. The oscillations in the photoemission intensity revealed the evolution of the QW states in the energy-thickness plane. Contrary to our expectations, QW-state energy increased with film thickness. The result was quantitatively explained using the so-called phase accumulation model. We also developed double wedged samples, which enabled us to explore the interference between two QWs.
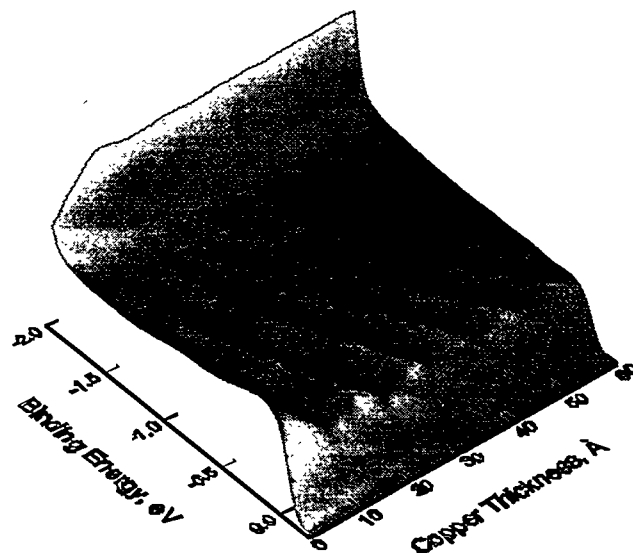
Figure 1. QW states obtained from photoemission on wedged Cu film.

Publication

R.K. Kawakami, E. Rotenberg, E.J. Escorcia-Aparicio, H.J. Choi, T.R. Cummins, J.G. Tobin, N.V. Smith, and Z.Q. Qiu, "Observation of the Quantum Well Interference in Magnetic Nanostructures by Photoemission," *Phys. Rev. Lett.* **80**, 1754 (1998).

MSD Theory and NERSC Computation for ALS Experiments

Principal Investigator: Michel Van Hove

Project No.: 96042

Project Description

This project will lead to theoretical and computational support to nation-wide experimental users of LBNL's Advanced Light Source (ALS). The ALS exploits sophisticated, state-of-the-art facilities to produce a rapidly increasing amount of experimental data that requires advanced numerical treatment and simulation to yield scientifically useful results. Important information can thereby be obtained about the atomic-scale structural, electronic, magnetic, chemical, corrosive, tribological, and biological properties of surfaces and interfaces of

technologically relevant materials. Examples include electronic nanostructures, magnetic storage materials, chemical catalysts and sensors, corrosion protection, hard coatings, and biological membranes. To enable the timely interpretation of this and other data, the National Energy Research Scientific Computing Center (NERSC) is bringing massively-parallel computing methods and capabilities to bear on the theory being developed for this purpose by LBNL's Materials Sciences Division (MSD). This approach enables experimentalists to plan and simulate future experiments, rapidly evaluate and fine-tune ongoing experiments, and fully analyze and refine finished experiments.

This project develops and applies powerful theoretical and computational methods to deal with the complex electron multiple-scattering processes that underlie the experimental techniques used by many research groups at the ALS, including photoelectron diffraction and holography, x-ray absorption spectroscopies, and spectromicroscopies. Collaboration between MSD and NERSC staff leads to new approaches to maximize computational efficiency. Close interaction with ALS users enables the most effective application of these methods to extract technologically relevant information about a wide variety of materials. As a result, computational methods are implemented that utilize NERSC capabilities to tackle problems of unprecedented scale and open up the field to research on new classes of materials. Further extensions of existing methods and new techniques are introduced in response to input from ALS users.

Accomplishments

New Photoelectron Diffraction Code

A new code, the multiple scattering in cluster diffraction (MSCD) package, has been developed using the novel backward summing method within the Rehr-Albers approximation, which reduces computation time an order of magnitude in real simulations as compared to prior codes. By applying object-oriented programming, this code provides a better user interface (which is particularly important for convenient use by experimentalists), general data formats, and fully functional subsidiary utilities. These unique features save the user much time in data preparation and management. For more information on this package, see http://electron.lbl.gov/mscdpack/mscdpack.html.

The sequential version of this code has been implemented on supercomputers (under UNIX) and UNIX Sun workstations as well as on PC and Macintosh desktop computers. Comprehensive test calculations agree well with more exact (but much slower) calculations. The code has been parallelized under message passage interface (MPI) (facilitated by its object-oriented C++ programming) and ported to the NERSC Cray T3E. Extensive comparisons of code performance on the T3E and cluster of multiprocessor systems (COMPS) parallel architectures have been conducted under MPI.

This new code is currently being generalized to consider circular dichroism (effects obtained by contrasting measurements performed with right- versus left-circular polarized light from the ALS), spin effects such as magnetism (including magnetic circular dichroism), and relativistic spin flip. Demand for these capabilities is growing among ALS users, particularly for the study of novel magnetic materials.

Other Activities

The Fast Fourier Transform approach has been enhanced by NERSC's P. Tang to permit new and efficient methods for holographic reconstruction of 3D atomic maps of surfaces and interfaces—a valuable method to obtain structural and magnetic detail about materials. Work with J. Carter has also explored issues of parallelism. In a related project, our codes have been ported by S. Sachs and G. Stone to a COMPS to test the optimum utilization of the advanced architecture of a Network of Workstations (NOW), starting with the application of genetic algorithms.

Several active collaborations are extending the capabilities of our underlying theoretical methods. Collaborators include C.S. Fadley (LBNL and UC Davis), J. Menchero (LBNL and UC Berkeley), J.J. Rehr (University of Washington at Seattle), W. Schattke (University of Kiel), A. Chassé (LBNL and University of Halle), and F.J. García de Abajo and J. Osma (LBNL and University of San Sebastian).

In addition, we have started to interact with a number of experimental users of the ALS. Pre-experiment feasibility studies have been performed for the P.N. Ross group to explore the optimum conditions for studying substitutional adsorption systems with photoelectron diffraction at the ALS. Related quantum chemical calculations to obtain molecular

orbital information and core-level shifts for molecules adsorbed on metal surfaces have also been undertaken. In developing the MSCD code, we benefited from extensive collaborations with the C.S. Fadley group and application to various photoemission data measured at the ALS. Collaborations with the D.A. Shirley group (in which the backward summing method was initiated) benefited from application of our newer codes to the interpretation of other ALS photoemission data. Similar interactions have begun with the ALS group of B.P. Tonner, S.D. Kevan, E. Rotenberg, and J.D. Denlinger, producing considerable experimental data that await interpretation.

We have started a global effort to combine the capabilities of international synchrotron radiation theorists. This Synchrotron Radiation Research Theory Network (SRRTNet) will coordinate the efforts across synchrotron facilities through the Web and in a series of workshops. We hope to make our computer codes more user friendly, provide a seamless computing environment for experimentalists, and accelerate analysis time from measurement to publication. For further information, see http://electron.lbl.gov/srrtnet/srrtnet.html.

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Molecular Rulers for the Study of Synthetic and Biological Macromolecules in Aqueous Conditions

Principal Investigators: Shimon Weiss, Paul Selvin, Deborah Charych, and Peter Schultz

Project No.: 97025

Project Description

Advances in room-temperature, single-molecule detection and single-molecule spectroscopy by laser-induced fluorescence provide new tools for the study of individual synthetic and biological macromolecules under physiological conditions. Two properties of a single fluorescent probe attached to a macromolecule can be exploited to provide local structural information. The first is the very high sensitivity of the fluorophore to its immediate local environment, including sensitivity to the presence of other fluorophores and quenchers nearby. The second is its unique absorption and emission transition dipoles, which can be interrogated by polarized excitation light or by analyzing the emission polarization.

Using these properties, we developed single-molecule fluorescence-spectroscopy tools—"molecular rulers"—that can relay the conformational dynamics of single biological molecules to the physical observables. Fluorescence-resonance-energy transfer (FRET), which measures the proximity between two fluorophores, and fluorescence-polarization anisotropy, which reports on the fluorophore's rotational dynamics, can provide information on local structural changes. Single-molecule methods have important advantages over conventional ensemble measurements: (1) they can resolve and quantitatively compare distinct subpopulations of conformational states, otherwise invisible at the ensemble level; and (2) they can resolve dynamic conformational changes.

Accomplishments

Recently, we have demonstrated the ability to identify conformational states and separate subpopulations of individual macromolecules in a heterogeneous solution by ratiometric single-molecule-burst methods. We extended single-pair FRET (spFRET) to measure distributions in the energy-transfer efficiency of freely diffusing single molecules. A series of donor-acceptor DNA constructs with varying intra-molecular fluorophore distances was used to measure the mean and the distribution width of FRET efficiencies as a function of distance on the single-molecule level. Figure 1a shows photon bursts recorded from diffusing DNA molecules in a buffer. Bursts were simultaneously recorded on donor (in red) and acceptor (in black) channels. A histogram for energy-transfer efficiencies calculated from the burst data is shown in Figure 1b. It shows two peaks: the first peak, around zero transfer efficiency, resulted from donor-only-labelled molecules (the result of accelerated photobleaching of the acceptor) that can be discarded. The second peak, around unity transfer efficiency, resulted from molecules exhibiting large transfer efficiencies. This peak was shown to shift to lower transfer efficiencies as the donor-acceptor distance was increased, according to the dipole-dipole interaction $1/R^6$ distance dependence. Figure 1c shows a histogram of a sample containing a 1:1 mixture of double-stranded DNA with 7 and 14 base-pairs separation between donor and acceptor fluorophores. The two peaks around $E\sim0.7$ and $E\sim1$ prove that it is possible to identify and separate sub-populations according to their conformational states. We expect that single-molecule ratiometric-burst techniques will be suited for identifying, selecting, sorting, and sizing macromolecules in heterogeneous solutions, and thus for following the kinetics of biomolecular reactions such as protein folding.

Single-molecule equilibrium measurements can unravel dynamical information as well. Using intramolecular spFRET measurements on single SNase protein molecules, we observed interesting gradual fluctuations in FRET efficiencies. A combination of single-molecule polarization measurements, spectral-fluctuation measurements, and simulations showed that the observed FRET efficiency fluctuations originated for millisecond-scale conformational dynamics of the proteins themselves. Figure 2 shows anticorrelated fluctuations in donor- and acceptor-emission time traces, reflecting the protein's conformational dynamics. We also studied protein-inhibitor binding by single-molecule polarization and spFRET, finding that these methodologies are sensitive enough to distinguish between the ligand-free and inhibitor-bound states of the enzyme. The above observations could not be detected by conventional ensemble studies: the fluctuations would be averaged out because of the lack of synchronization among molecules.
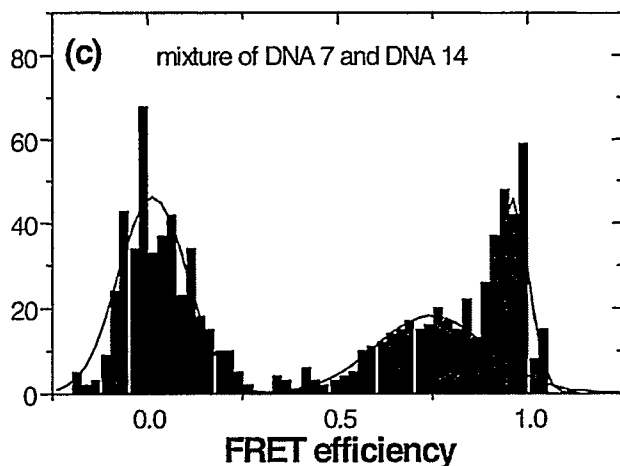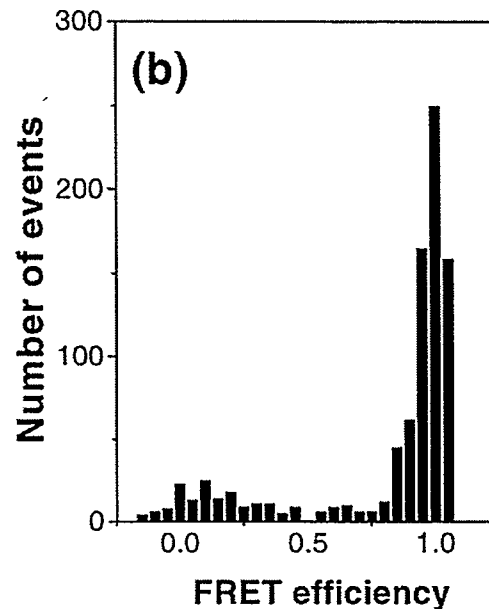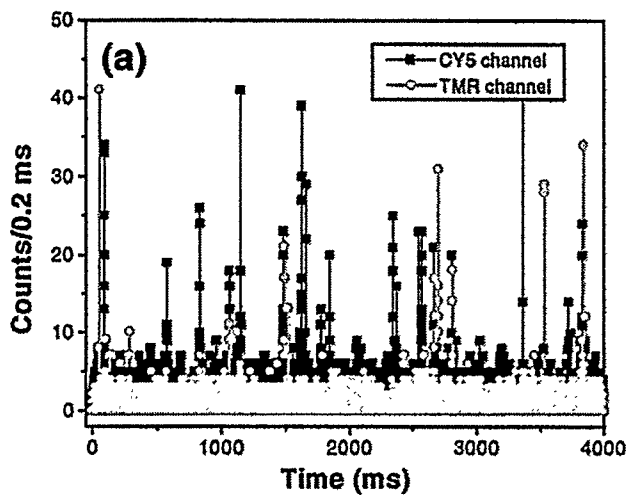
Figure 1. (a) Donor (in gray) and acceptor (in black) bursts of diffusing 40 mer DNA molecules in buffer. TMR is attached to the 5' end and Cy5 is attached 7 nucleotides apart. (b) A histogram of energy transfer efficiencies extracted from the bursts in (a). (c) Histogram of a sample containing a 1:1 mixture of 7 and 14 base-pairs separation dsDNA, demonstrating the ability to separate sub-populations.
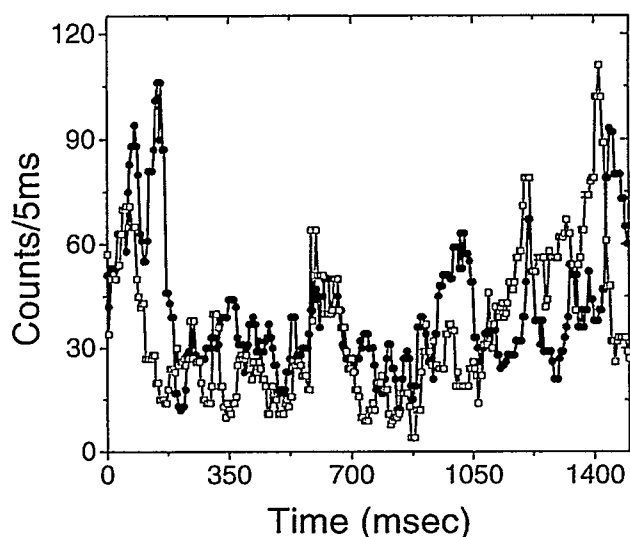
Figure 2. Donor (indicated by solid squares) and acceptor (indicated by circles) emission time traces of a doubly-labelled TMR/Cy5 SNase molecule immobilized on glass in buffer. The large and gradual fluctuations in I_d and I_a report on protein structural fluctuations on the milliseconds time scale.

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Femtosecond X-Ray Spectroscopy at an ALS Beamline

Principal Investigators: Robert Schoenlein, Alexander Zholents, Max Zolotorev, and Philip Heimann

Project No.: 98023

Project Description

The goal of this project is to develop a novel technique for generating femtosecond x-ray pulses from the Advanced Light Source (ALS). This is the first attempt to extract femtosecond pulses directly from a synchrotron storage ring and will improve the temporal resolution available at an existing bend-magnet beamline from 30 ps to ~250 fs. High brightness femtosecond x-rays will allow researchers to apply powerful x-ray structural probes such as diffraction and extended x-ray absorption fine structure with ultrafast time resolution. This development promises to open new areas of research in physics, chemistry, and biology by allowing the motion of atoms in materials to be directly probed on the time scale of a vibrational period, which is the fundamental time scale for, e.g., structural dynamics, chemical reactions, and phase transitions. In addition to significantly enhancing the ALS, this project will help develop a fourth-generation synchrotron light source, providing two to three orders of magnitude improvement in time resolution over existing synchrotron sources.

The temporal duration of synchrotron light pulses is determined by the duration of the stored electron bunches (typically ~30 ps). We propose to reduce the duration of the x-ray pulses by more than two orders of magnitude by selecting radiation that originates from a thin (~100 fs) temporal slice of the electron bunch. Figure 1 illustrates how such a slice can be created through the interaction of a femtosecond laser pulse co-propagating with an electron bunch in an appropriate wiggler. The high electric field of the laser pulse modulates the energy of a slice of the electron bunch (see Figure 1A). The accelerated and decelerated electrons are separated from the main electron bunch by a bend magnet (see Figure 1B). Femtosecond x-rays are generated at an existing beamline by imaging the synchrotron radiation from the displaced femtosecond electron slice (see Figure 1C).
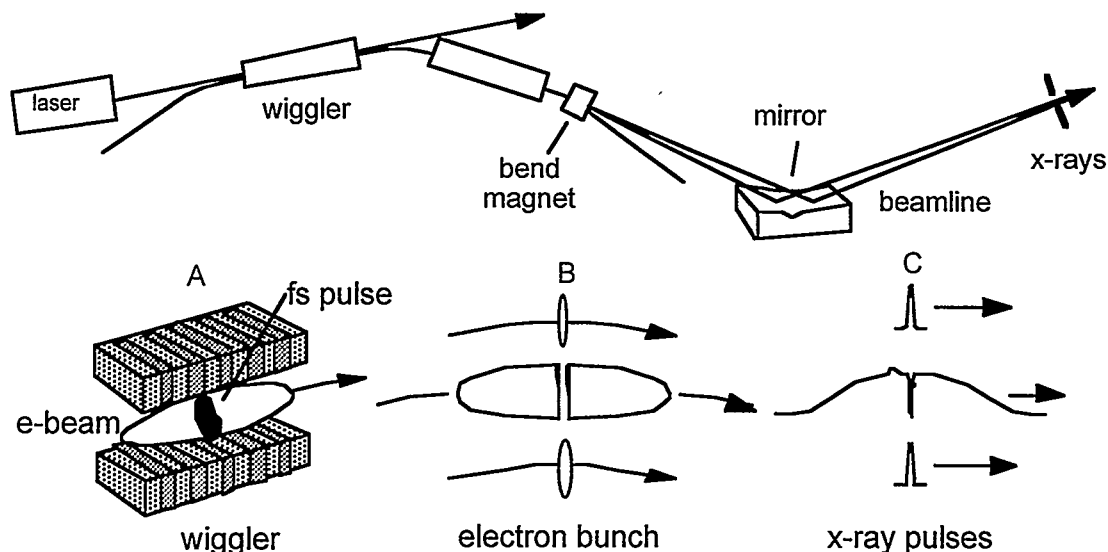
Figure 1. Schematic of technique for generating femtosecond pulses of synchrotron radiation.

Accomplishments

Considerable progress has been made toward the development of this source. The major components for generating femtosecond x-rays at the ALS are in place, including a femtosecond laser synchronized to the storage ring, beam transport optics, and diagnostics for monitoring the interaction between the laser and the electron beam. The quality of the laser/e-beam interaction is evaluated by measuring the gain experienced by the laser beam passing through the wiggler. This is the same gain mechanism that is active in free-electron lasers. The good agreement between the measured gain and theoretical predictions (based on known parameters of the electron beam) demonstrates that the interaction between the laser and the electron beam is nearly optimal.

We have recently made the first measurements of femtosecond synchrotron radiation from ALS Beamline 6.3.2. This was accomplished by cross-correlating visible light from the beamline with ~50 fs pulses from the laser in a nonlinear crystal. Figure 2 shows such a cross-correlation on a long time scale. The measured pulse width ($\sigma = 16$ ps) corresponds to the electron bunch duration.

Inset in Figure 2 is a high time-resolution measurement of the central core of the bend-magnet radiation, which is selected using a pair of slits in the image plane. A femtosecond "dark" pulse, which appears as a narrow notch in the main pulse, is clearly resolved. This dark pulse is a consequence of the displacement of a femtosecond slice of electrons from the central part of the electron beam due to interaction with the ultrashort laser pulse (see Figure 1).

The initial observation of femtosecond synchrotron radiation is a significant first step in the development of a dedicated beamline for femtosecond x-rays spectroscopy at the ALS.

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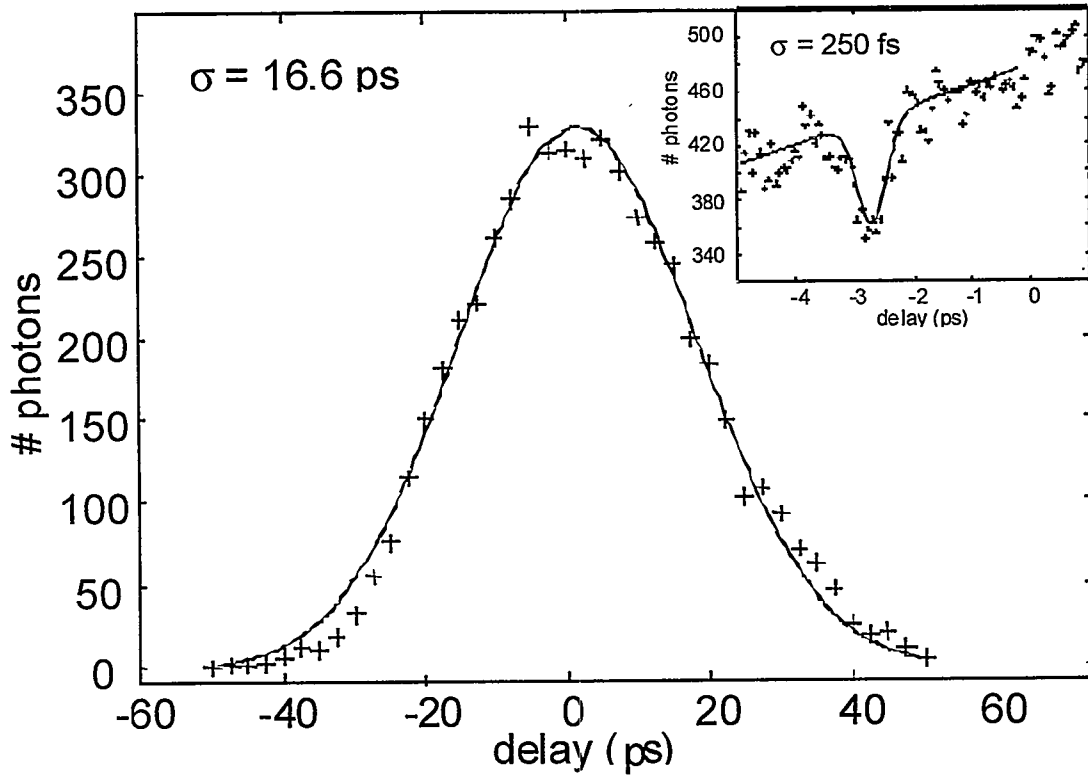
Figure 2. Cross-correlation measurement of visible synchrotron pulse with 50 fs laser pulse. Inset: femtosecond dark pulse from e-beam slicing.

Nuclear Science Division

Berkeley Experiments with Accelerated Radioactive Species at 88-Inch Cyclotron

Principal Investigator: Joseph Cerny

Project No.: 98024

Project Description

The goal of the Berkeley Experiments with Accelerated Radioactive Species (BEARS) project is to study a radioactive ion beam (RIB) capability at LBNL's 88-Inch Cyclotron. Nuclear scientists around the world are greatly interested in the opportunities provided by RIBs. The 1996 Nuclear Science Advisory Committee (NSAC) long-range plan for nuclear physics lists the development of a national RIB facility as its highest priority after the completion of the Relativistic Heavy Ion Collider (RHIC) at Brookhaven National Laboratory (BNL). Aside from providing a new research tool at the 88-Inch Cyclotron, the work being done for the BEARS initiative may provide critical research and development for this national facility.

The BEARS project is made feasible by the presence of two existing cyclotrons at LBNL. The radioactive species to be accelerated will be produced by the Biomedical Isotope Facility (BIF) cyclotron, a 10 MeV proton accelerator located approximately 300 m uphill from the 88-Inch Cyclotron. Radioactive isotopes are produced from (p,n) and (p,α) reactions and will be transported via a 300 m capillary to the 88-Inch Cyclotron. There, the activity will be separated from carrier gas, injected into an electron cyclotron resonance (ECR) ion source, and then accelerated by the 88-Inch Cyclotron. Beams of ^{11}C and ^{14}O will be made available using this technique in the coming year.

All components of the BEARS system (for activity production, activity transport, gas removal, ionization, and acceleration) are based on established techniques. The challenge lies in combining these techniques with sufficient efficiency that radioactive beams of usable intensity and purity result.

Additionally, safe transport of the radioactivity between the two cyclotrons is required.

Accomplishments

Initial work on BEARS focused on testing and optimization of each of the system components listed above. Production yields were measured, using both gas and solid targets. For production of ^{11}C and ^{14}O, a gaseous nitrogen target was found to give the highest yield. The transport times through 300 m of capillaries of various diameters were measured; transport may be accomplished in less than 60 s.

Two different techniques were tested for the removal of carrier gas from the radioactive isotopes. Immediately after production, both ^{11}C and ^{14}O form radioactive CO_2 gas through reactions with trace CO and O_2 in the N_2 target gas. Cryogenic trapping at liquid nitrogen temperatures may be used to collect this CO_2 while the nitrogen target gas is pumped away. The trap is then heated to release the radioactivity into the ECR ion source. A second gas-removal method uses aerosols in the carrier gas to which the radioactivity attaches; on exiting the capillary, the forward-moving aerosols pass through a series of holes separating chambers at increasingly higher vacuum. The light carrier-gas molecules do not pass through the holes as efficiently and are pumped away. This technique was tested extensively and may be used in the future with heavier, nongaseous radioactive species.

Work on the final two steps in production of the beams, ionization, and acceleration of the activity has focused on optimizing the tunes of the ECR ion source and 88-Inch Cyclotron, respectively. Because of the low intensity of these beams relative to stable beams, development of diagnostics for these systems has been challenging.

In initial tests, activity was produced at the 88-Inch Cyclotron and transported a short distance to its advanced ECR source, where the carrier gas was removed before ionization. These tests demonstrated that the gas could be removed successfully with a transport and trapping efficiency of 30–50%. Excellent ionization efficiencies as high as 11% and 3.6%, for $^{11}C^{4+}$ and $^{14}O^{6+}$, respectively, were also achieved.

In September, nearly the complete BEARS system was tested, using a "batch-transfer" method. Carbon-11

activity was produced at the BIF cyclotron and transported by truck to the 88-Inch Cyclotron in a lead-shielded container. After residual gas was pumped away using the cryogenic trapping method, the activity was ionized and accelerated to 100 MeV by the 88-Inch Cyclotron. This first attempt at producing a radioactive beam yielded an intensity of $\sim 3 \times 10^7$ ^{11}C ions per second. This result is comparable to the ^{11}C beam intensity available at the Louvain la Neuve RIB facility in Belgium, which currently holds the world record for this beam. The energy of the LBNL beam (100 MeV), however, was significantly higher than can be produced there. This experiment was successfully repeated in October. These results lead to a projected ^{11}C beam intensity of at least $\sim 10^8$ ions per second when the activity transfer line is completed. The first BEARS experiment, which will measure ^{197}Au(^{11}C, xn)$^{208-x}$At excitation functions, was begun in November 1998, again using this batch-transfer method to produce the beam.

Progress has also been made on the activity transfer line, which will consist of a bundle of capillaries encased within a 5 cm diameter tube in which a modest vacuum is maintained. Radiation detectors will continuously monitor the exhaust from the vacuum pump; if a capillary burst, it would be detected immediately and activity transfer would automatically shut down. A 15 cm diameter PVC pipe will surround this tube and protect it from the elements. Ten access boxes, spaced at regular intervals along the PVC pipe, will contain radiation detectors to monitor the transfer of activity. In FY98, the outer containment pipe, supports, and access boxes were built between the two buildings. The transfer line will soon be brought into each building; at the BIF cyclotron, this will involve trenching under a roadway. The transfer line should be completed by Spring 1999.

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The collaboration maintains a BEARS web page, where updates are regularly posted. See http://cerny3.lbl.gov/BEARS/homepage.html.

Research Opportunities with 8π Spectrometer Array at 88-Inch Cyclotron

Principal Investigators: I-Yang Lee, Lee Schroeder, and David Ward

Project No.: 98025

Project Description

The 8π Spectrometer, on loan from McMaster University, has been operating in Cave 4C at the 88-Inch Cyclotron since April 1998. The instrument is made up of a high-quality Bismuth-Germanate (BGO) spherical shell of 72 detectors and an array of twenty HPGe detectors with BGO Compton-Suppressor

shields. A number of auxiliary detectors and special equipment developed for the spectrometer have also been employed, including the computer-controlled recoil-distance apparatus. The MINIBALL array of 45 CsI detectors, which was on loan to Oak Ridge National Laboratory, has been returned and is essentially ready for experiments.

In FY98, a vigorous research program was conducted on the 8π Spectrometer. Some 14 experiments approved by the PAC were carried out, involving 29 scientists and 12 students from 13 institutions.

Accomplishments

Study of Neutron-Rich Nuclei with Target-Fragmentation

In this experiment, a ^{12}C beam at 30 MeV/A bombarded a natural (51 V) target. At this energy, a significant cross section was expected to fragment, leading to exotic, neutron-rich species with A < 50. The results of this first-try experiment were very encouraging. They indicated that this configuration could be a powerful method for spectroscopy of exotic species, complementary to the technique employed at Michigan State University (and other laboratories) where the exotic species is first produced by fragmentation (a 51-V beam in this example) and then excited in a secondary reaction.

Jacobi Shapes

The equilibrium shape of a rotating fluid undergoes an abrupt transition to super-deformed configurations above a certain critical angular momentum. These Jacobi-like configurations are caused entirely by centrifugal forces and are predicted to appear only at very high angular momenta in nuclei that can support such angular momenta without fissioning. We searched for this effect in the reactions of a ^{48}Ca beam on targets of ^{50}Ti, ^{64}Ni, and ^{124}Sn. This latter system was not expected to show any effect because it is too fissile; nevertheless, it was included to provide a reference point. The technique was to record HPGe spectra in coincidence with the hit pattern in the BGO ball. In the gamma-ray spectrum for each system, a very strong bump, characteristic of rotational transitions at very high spin, was observed (Figure 1). We examined the differences between HPGe spectra gated on successive numbers of hits (K) registered in the BGO ball. With an appropriate normalization, the difference between spectra gated on (for example) K+1 and K hits is representative of the spectrum of the "new" transition added to the top of the rotational-like cascade. A Jacobi effect will then show up as a shift in the difference spectra from the bump-edge energy (characteristic of the normal nuclear shape) to lower energies (characteristic of a more deformed shape).

The imperfect response of the HPGe detectors and of the BGO ball considerably complicates any quantitative analysis of these difference spectra. We have therefore taken the approach that experimental results will be compared with a simulation that filters the nuclear-structure information through the measured response functions of the instrument. Initial results have been very encouraging and suggest that detailed structure information can be obtained at very high spin.
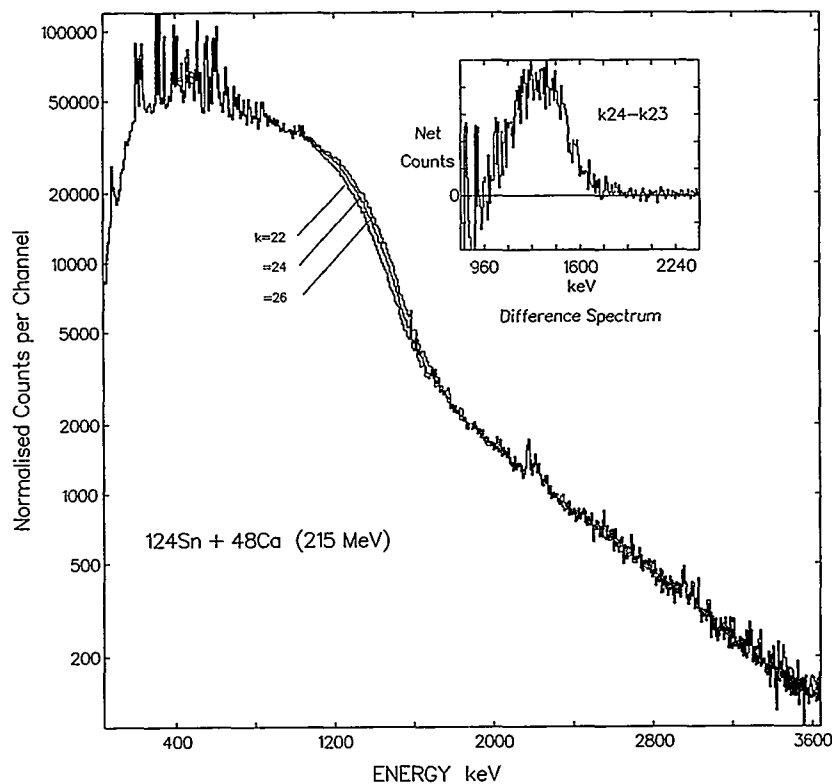
Figure 1. Spectra recorded in the Compton-suppressed HPGe detectors of the 8π Spectrometer gated on the number of hits, K, registered in the BGO ball. The sharp rise in the spectrum beginning at about 1600 keV and ending at about 1000 keV is a characteristic of nuclei at high spin and marks the so-called E2 bump region where the gamma-ray flux passes down many unresolved rotational bands. By gating on K, we select from the ensemble nuclei populated with increasingly higher angular momentum, and the bump-edge is seen to move to higher gamma-ray energies. With some reservations (as discussed in the text), a difference spectrum, of the type shown inset, measures the spectrum of the "new" transitions selected by the higher K-value.

Distributed Construction and Analysis of Multidimensional Gamma-Ray Coincidence Databases

Principal Investigators: Mario Cromaz, James Symons, Randy Macleod, and I-Yang Lee

Project No.: 97027

Project Description

This project seeks the development of software to allow analysis of high-fold gamma-ray coincidence data acquired using new detector arrays such as GAMMASPHERE. This new generation of gamma-ray spectrometers is able to record large samples of four- and higher-dimensional coincidences for which signal-to-noise ratios are greatly enhanced. Unfortunately, analysis programs available to physicists working in this field are restricted to two- or three-fold coincidences. These programs cannot be extended to higher dimensions in a straightforward manner because of fundamental limitations in the algorithms and storage techniques used.

Our approach to this problem can be divided into two parts. Our first goal is to develop techniques that allow storage and retrieval of very large numbers of events. Our second goal is to develop analysis techniques that can locate correlations in these data, which can then be used to investigate novel aspects of nuclear structure.

Accomplishments

One aspect of the project is to develop an efficient database for the storage and retrieval of the large, multidimensional datasets required for the analysis of experiments using modern gamma-ray spectrometers such as GAMMASPHERE. For low dimensionality (fold less than four), histograms are the preferred method of storage. For fold greater than four, however, the storage requirements for histograms become prohibitively large. GAMMASPHERE experiments already generate large numbers of events with fold greater than four, and events of this kind will dominate the data acquired by spectrometers planned for the future.

Assuming that storage is available for the high-fold data, the next problem is to retrieve specific events at the part-per-million level for further analysis. Without an indexing scheme for the data, this task is prohibitively slow, and it can be shown theoretically that no method can ensure that all events that are close to one another in Euclidean space will be close to one another on the storage medium. We have achieved a practical solution to this problem by developing a hierarchical, adaptive database that stores the events in buckets whose volume is inversely proportional to the local-phase-space density. Preparing the database is time consuming (although no more so than preparation of the histograms used by current analysis techniques), but once prepared, interactive data analysis can proceed with queries being submitted to the database to return subsets of the events. Performance of the database is excellent, and the program is now being used for superdeformed-band searches and level scheme analysis.

We have also continued to develop analysis tools for high-fold events. A program to search for clusters in five- and higher-dimension data has been written, tested, and used to locate new superdeformed bands in the ^{150}Gd and other nuclei. One issue remaining to be addressed is the proper evaluation of the background in high-dimensional space. We are also interested in developing software to automatically construct level schemes.

Publications

This work was presented in an invited talk to the American Chemical Society. A technical paper describing this work is now in preparation for submission to *Nuclear Instruments and Methods*.

Physical Biosciences Division

Stochastic Logic in Biochemical and Genetic Reaction Networks: Theory and Experiment with Application to Bacterial Pathogenesis

Principal Investigator: Adam Arkin

Project No.: 98026

Project Description

An organism's genome is commonly considered to be the program, executed by biochemistry, that defines the organism's behavior and development. It would be inaccurate, however, to attribute a computer-like "logic" to the decisions made by this program. In fact, the chemical reactions set off by this "computer" are highly nonlinear and do not obey the laws of Boolean logic. Qualitative analysis of their behavior as a network is made even more difficult because these reactions involve concentrations of molecules of less than 100 molecules per cell and share substrates, products, and effectors. This difficulty is exacerbated by the small numbers of molecules involved in these reactions. From physical first principles, thermal fluctuations in reaction rates are expected to become significant in comparison to average behavior at such low concentrations. Because reactions involving genetic control generally involve only one or two copies of the relevant promoters and genes per cell, these "noise" fluctuations are likely to be greater for these reactions.

In prior work, we have examined some detailed mechanisms of gene expression in prokaryotic systems and confirmed, theoretically, that the temporal pattern of protein production from a single gene in a growing cell is highly erratic for a wide range of experimentally observed kinetic parameters. If our theoretical analysis is correct, the immediate questions raised by this observation are: "How is the genetic program executed correctly if its elementary components are so noisy?" and "Are any organism's genetic programs set up to exploit this noise and achieve diversity in its behavior or the population as a whole?"

The developmental program encoded by the hosts genome is designed, in large part, to throw the right set of genetic switches at the right times and places in order to produce particular cell types in an organism. To understand the common regulatory architectures that are used to construct these developmental switches, we have focused on the study of two genetic "switches": the bacteriophage lambda lysis/lysogeny decision and random phase variation of type-1 pili expression in *Escherichia coli*. The architecture of these two switches, one implemented by two antagonistic feedback loops and the other implemented by a DNA inversion reaction, is typical of a large class of developmental switches commonly found in pathogenic microorganisms (as well as in general developmental pathways). Our theories predict that the significant noise expected in the elementary genetic reactions will lead to a statistical divergence in cell fate even with identical initial conditions. We wish to experimentally confirm this prediction and explore the role of genetic noise in promoting the virulence of these particular organisms.

Our first goal is to build computational toolkits to (1) database the large amount of heterogeneous biological data necessary for building and validating the biological models needed to understand these systems; (2) create biologist-friendly model-building interfaces to this database; (3) design and build the tools for network analysis (e.g., stoichiometric network analysis, sensitivity analysis) and simulation (e.g., for hybrid stochastic, ordinary differential, algebraic, and spatially-dispersed systems); and (4) design and build visualization and reporting tools for digesting the complex time and space resolved output from the simulation programs. Our second goal is to apply these tools to the engineering analysis of the genetic switches described above.

Accomplishments

During this first year, the laboratory infrastructure for both the computation and theoretical sides of this project were built. This involved purchase of computer systems, outfitting of the molecular biological laboratories for performing these studies, and hiring of personnel to work on various parts of the project.

Work on the computer-aided simulation and analysis tool (now called BIO/Spice) progressed into its

second stage. A new algorithm for simulating multi-time scale chemical kinetic systems that allows dynamic switching between (computationally expensive) stochastic integration and (more efficient) deterministic integration was devised and implemented. Under development in collaboration with H. McAdams at Stanford University and D. Gillespie at the China Lake Air Warfare Base, this technique relies on (1) approximating the underlying jump Markov process (the chemical master equation) by a continuous Markov process and then (2) simulating that process according to its Langevin equation. The front-end graphical user interface has been prototyped in Java to a point that allows the rapid construction of nonspatially extended, fully stochastic biochemical and genetic reaction networks. The front-end interface can contact simulation kernels running on remote machines to execute the calculations. It also interfaces to a (currently small) local database of biochemical reaction network structures, chemical mechanisms, and kinetic parameters.

An initial model and analysis of lambda-phage infection of E. coli has been completed and published. Our conclusion is that stochastic events play an important role in the decision processes and lead to inevitable population heterogeneity both in cell fate and time-to-fate commitment. The model is validated in comparison to a number of experimental data. Further work on the theory of stochastic gene expression, regulatory network motifs and signal processing, and the reliability engineering of biological systems is ongoing.

In support of the type-1 pili phase variation project, pilot studies have been completed to test simulations of the kinetics for DNA inversion, chemotaxis, and adhesion of E. coli to epithelial sheets, cell growth and division, and colony formation and infection spread. Initial results indicate that differences in the rate of individual cellular switching times and the average fimbriation of the population can lead to significant differences in spread and colonization of the E. coli population on model epithelial sheets. Different clinical isolates, with different virulence indices, have different fimbriation kinetics. We are now attempting to correlate model results with our clinical results.

Publications

A.P. Arkin, "Signal Processing by Biochemical Reaction Networks," *From Molecules to Dynamical Diseases*, J. Walleczek, ed. (Cambridge University Press, 1999).

H.H. McAdams and A.P. Arkin, "Genetic Regulation at the Nanomolar Scale: It's a Noisy Business!," *Trends in Genetics* (1999).

A.P. Arkin, J. Ross, and H.H. McAdams, "Stochastic Kinetic Analysis of Developmental Pathway Bifurcation in Phage Lambda-Infected E. coli Cells," *Genetics* 149(4), 1633–1648 (1998).

H.H. McAdams and A.P. Arkin, "Simulation of Prokaryotic Genetic Networks," *Annual Rev. Biophys. Biomol. Struct.* 27, 199–224 (1998).

GEOCORE: Development of a Protein Folding Algorithm

Principal Investigator: Kenneth Dill

Project No.: 98042

Project Description

This project addresses the "protein folding problem" by developing GEOCORE, a new computer algorithm intended to predict the folded structures of proteins from their amino-acid sequences. During the past 30 years, dozens of computer algorithms have been designed that attempt to fold proteins. None has yet succeeded. There is general agreement that a successful algorithm will ultimately solve two problems: (1) it will have a proper free-energy function combined with a suitable chain representation, and (2) it will have a very fast conformational search strategy.

GEOCORE is a new approach to computational protein-folding methods. It is based on a very extensive conformational-sampling method (branch-and-bound) that explores essentially all the conformations that might include the global minimum in free energy. This method is the first to show that such complete sampling is practical for peptide folding. GEOCORE uses a simple energy function involving united atoms, steric repulsion, and hydrophobic and hydrogen-bonding interactions. This project aims to (1) refine the energy, (2) develop a "smart" search strategy to construct tertiary structures from secondary structures, and (3) test it on peptides and proteins.

Accomplishments

During the initial three months of this project, we have begun development of the smart search strategy. When the chain-growth method grows a piece of secondary structure (helix or strand), the new algorithm searches to ascertain whether it can be docked onto nearby structures that have already been laid down. If so, the algorithm uses the analytical method of Go and Scheraga to compute the bond angles needed by the intervening loop and give a canonical tertiary packing.

A Global Optimization Strategy for Predicting Protein Structure

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Principal Investigator: Teresa Head-Gordon

Project No.: 96038

Project Description

This project focuses on the prediction of protein native structure given the amino acid sequence as input. The availability of high-performance computing on the T3E, J90, and C90 at NERSC allows us to define the following three goals: (1) to develop the ability to characterize the energy surface by determining the global minimum and all relevant low-lying minima using sophisticated mathematical optimization techniques; (2) to provide the best approximation to this energy surface beyond what is available today; and (3) to predict protein structure in the size range up to 1000 atoms, comparable to small globular proteins of 50–100 amino acids.

We seek development of highly effective optimization strategies for tackling the protein-structure prediction problem. Our approach is to first broadly sample conformational space using neural network and Hidden Markov Model predictions and then apply different global-optimization approaches to these diverse set of starting structures. We will use promising global optimization methods, including stochastic/perturbation, smoothing, and structure-prediction biasing. A concurrent consideration is to improve protein-solvent force fields. The first is the

derivation of spherically averaged hydration potentials of mean force between amino-acid side chains from molecular-dynamics simulation in collaboration with neutron scattering experimentalists. These "implicit" water models (intended for the study of protein structure prediction) strike a good balance between physical complexity and computational simplicity.

Accomplishments

We are developing a joint global optimization approach (based on sampling, perturbation, smoothing, and biasing) that has been quite successful working directly on the potential energy surfaces of small homopolymers, homopeptides, and (recently) α-helical proteins. Our overall strategy is to make good predictions of secondary structures by neural network techniques and then manifest them as soft constraints to use within a local optimization algorithm and as guidance within a global optimization framework. The use of soft constraints permit partial solution of the global optimization problem within a local optimization context by quickly refining α-helices and β-sheets when they are predicted with even moderate accuracy. The small-subspace global optimization techniques will be concentrated on regions predicted to be coil (a category for which it is not possible to define a soft constraint) and should be particularly effective in resolving these regions.

The developed strategy was parallelized and run on the T3E at NERSC using between 16 and 128 processors. In the last year, we have explored different parameterizations of the global optimization methods and tested their effectiveness on the prediction of a 70-amino-acid protein, uteroglobin (Figure 1). We have just begun a second all-helical target of 104 amino acids and will be testing the robustness of our optimization approach on several
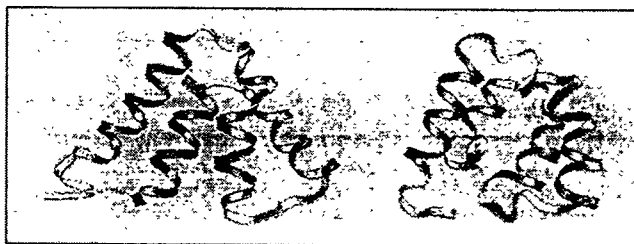

Figure 1. Global optimization prediction from sequence (right) and crystal structure (left) of the a-chain of Uteroglobin.

more helical protein targets. We have received follow-on funding from DOE to tackle the more difficult folding class of β-sheet proteins this year. One paper and several abstracts have been submitted for conferences relating to this work. In addition, we have developed a visual demonstration of this work with T. Ligocki, which S. Crivelli presented at the highly visible Supercomputing '98 meeting.

Publications

S. Crivelli, Phillips, Byrd, Eskow, Schnabel, Yu, and T. Head-Gordon, "A Global Optimization Strategy for Predicting Protein Tertiary Structure: ?-Helical Proteins" (submitted to Proteins: Structure, Function Genetics, 1998).

Byrd, S. Crivelli, Eskow, T. Head-Gordon, and Schnabel, "Predicting Protein Tertiary Structure using a Global Optimization Algorithm with Smoothing," SIAM Conference on Optimization (1999).

S. Crivelli, Phillips, Byrd, Eskow, Schnabel, Yu, and T. Head-Gordon, "A Global Optimization Strategy for Predicting Protein Tertiary Structure: ?-Helical Proteins" (presented at Supercomputing '98).

"Basis Set" of Protein Folding: A Foundation for Functional Genome

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Principal Investigator: Sung-Hou Kim

Project No.: 98027

Project Description

The goal of this proposal is to identify the "basis set" of proteins in an organism and determine their three-dimensional structures to establish a foundation for discovering the functions of the proteins predicted by the genome sequence. It is widely accepted that all proteins in an organism may belong to a finite set of folding classes, the "basis set," or some linear combination of the members of the basis set. As a test system, we chose *Methanoccocus jannaschii*, a hyperthermophile, whose entire genome has recently been determined.

The majority of the 1738 genes from *M. jannaschii* code for proteins. These genes will be clustered into a

smaller number of families based on the homology among protein sequence and folds. For this purpose, a computational method will be developed to predict fold similarities even in the absence of sequence similarities.

Accomplishments

A survey of all known three-dimensional structures of proteins suggests that most of the folding domains appear to be composed of about 100 amino acids or more. Because the average protein contains about 300 amino acids, a sliding window of 100 residues with sliding-step size of 50 residues gives 5 possible 100-residue sequence domains. For about 1700 protein sequences of *M. jannaschii* [(5 × 1700) × (5 × 1700)], possible pair-wise sequence alignments are needed, which is about 72,000,000 alignment calculations. Once 72-million alignment scores are calculated, they will be clustered based on the similarities of the domain sequences. Because we do not know a priori the size and location of a domain in a protein, several different criteria must be tested to obtain the optimum domain size and location search step of the domain. One member from each cluster is collected to form the "Sequence Basis Set."

For each member of a given cluster, our search will use existing databases for any homologous proteins in other organisms for which their biochemical functions are known. If found, the function of the proteins in that cluster will be tentatively assigned to those functions found in homologous proteins from other organisms.

To simplify these processes, we are in the process of developing a new algorithm to predict whether two sequences with no significant sequence similarity will have the same or similar 3-D fold. We have developed a new and novel method, which is currently being tested and tooled up for large-scale testing on the National Energy Research Scientific Computing Center 512 processor computer T3E.

Enclosure for Ambient Environment XAS Studies at ALS Beamline 9.3.1

Principal Investigators: Melvin Klein and Vittal Yachandra

Project No.: 98043

Project Description

The purpose of this proposal is to provide a facility with general user access for performing x-ray absorption spectroscopy (XAS) of lower-Z elements at the Advanced Light Source (ALS). Elements from P through Ca have K-absorption edge energies between 1.8 and 4.9 keV, whereas the L-edges of most second-row elements also fall in this range. The XAS, especially the near edge spectra of the lower Z elements, is extremely rich and can provide detailed chemical and structural information (especially chemical speciation) on samples as diverse as biological cells and geological samples. Such measurements can be performed on any state of matter at selected temperature and environment. The facility we propose will provide an enclosure with provisions for sample containment in an environment of the experimenter's choice (vacuum or specific atmosphere, elevated or reduced temperature, absorption or fluorescence detection).

We will construct a "mini-hutch" to safely contain general and specific components for XAS. Required components include detectors to monitor incident and transmitted photon flux, fluorescence, sample mounting, cryostat and other enclosures for achieving low or elevated temperatures, vacuum or other ambient gases, sample positioning, and alignment. Longitudinal positioning along the beam direction will provide for operation at or displaced from the beam focal position to permit examining a small or distributed fraction of a large sample.

Accomplishments

The primary emphasis of this project was to be able to perform XAS experiments at the sulfur and chlorine K-edges, 2.4 and 2.8 keV, respectively, on biological samples. (The U.S. lacks facilities for such work.)

After funding in late FY98, we arrived at a conceptual design of the end station (Figure 1). Appropriate
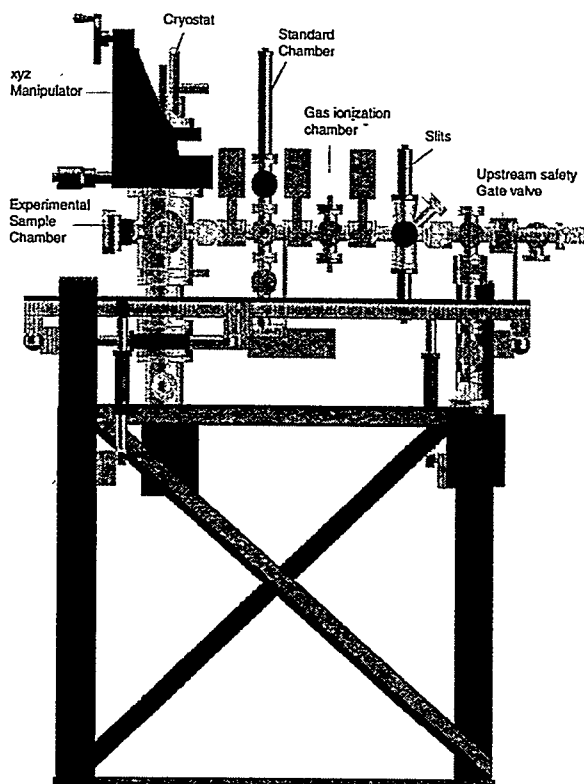

Figure 1. Endstation for soft x-ray absorption spectroscopy on biological samples.

Figure 2. Stand, struts, and top plate completed as of mid-November 1998. Ready for assembly of end station chambers, valves, slits, and other components.

reviews for operational and safety considerations were held, and a final design was approved. Components were listed for purchase or fabrication and were received by the end of FY98.

Under the able management of K.L. McFarlane, a new postdoctoral fellow in the group, fabrication of the experimental chamber, support stand, and structure have been completed (Figure 2). Tests on the system are to be completed in FY99.

Publications

K.L. McFarlane, M. Swanson, N. Hartman, Z. Hussain, V. Yachandra, and M.P. Klein, "An End Station for Soft X-Ray Absorption Spectroscopy of Biological Samples in a Controlled Environment," ALS Users Meeting, poster presentation (October 22–23, 1998).

Computational Modeling of Protein Folding and Unfolding Using Lattice Models and All-Atom Molecular Dynamics

Principal Investigator: Daniel Rokhsar

Project No.: 98044

Project Description

The goal of this project is the construction of quantitative theoretical models of biological materials and systems. Our primary focus will be two-fold: (1) the thermodynamic and kinetic properties of proteins and (2) the development and organization of neuronal networks in the visual system.

Studies of protein folding require extensive Monte Carlo simulation for thermodynamic properties and molecular dynamics and Langevin analysis for kinetics. Because all-atom calculations are limited to nanoseconds of real time (while real proteins fold in milliseconds), progress demands the construction of faithful, yet tractable models to make the best use of available computational resources. We use lattice models, simplified representations of proteins, and all-atom molecular dynamics with solvent to study the nature of folding and unfolding trajectories.

Simulation and analysis of retinal and cortical patterns and their formation require both image processing and dynamical simulations. Parallel simulation of a range of control parameters of these realistic neuronal networks is the best way to accumulate sufficient data to understand these complex dynamical systems. The goal of this effort is (1) a quantitative model of the developing mammalian retina and (2) the ability to make specific predictions for the behavior of this network under various conditions.

Accomplishments

Folding Pathways

We have studied the folding of protein-like heteropolymers by direct simulations of a lattice model that folds rapidly to a well-defined native structure. The details of each molecular folding event depend on the random initial conformation as well as random thermal fluctuations of the polymer. By analyzing the statistical properties of hundreds of folding events, we can find a classical folding pathway for such a polymer, which includes partially folded, on-pathway intermediates that are shown to be metastable equilibrium states of the polymer. These results illuminate the debate between the "classical" and "new" views of folding.

Beta Hairpin

Using all-atom molecular dynamics, we have examined the unfolding pathway of a beta-hairpin fragment of protein G. Although this fragment is small, it possesses many of the qualities of small proteins: secondary structure as well as a hydrophobic core determined by tertiary contacts. The unfolding pathway is constructed by obtaining an ensemble of unfolding trajectories at high temperature, using the Cray T3E at NERSC. We find that this unfolding pathway exhibits a series of discrete steps, each representing the dissolution of a specific aspect of the structure. These steps are characterized statistically.

Nature of Transition State for Folding

Using lattice simulation methods, we have completely analyzed the folding pathway of five model proteins. Our analysis explicitly constructs the transition state ensemble using the "p-fold" method we have developed, a computationally intensive but completely parallelizable algorithm for identifying

transition-state conformations that we have implemented on the Cray T3E at NERSC. By analyzing the structures of these conformations and comparing them with simulations of the principal experimental technique for studying transition states (phi-analysis method), we can understand the principal events of folding and how they are reflected in experimentally measurable quantities.

Retinal Wave Dynamics

We have developed a new model for the initiation, propagation, and termination of waves in excitable networks of neurons. Unlike as for earlier models, we analyze the wave in terms of a local network property of the system: the fraction of refractory cells in the vicinity of a given location. Using this coarse-grained description, we can quantitatively describe the waves in the developing mammalian retina. The various regimes of the model are discussed and related to other neural systems that display wave behavior. Based on our model, predictions can be made for the change in wave behavior due to pharmacological manipulations of the retina.

Publications

V.S. Pande and D.S. Rokhsar, "Folding Pathway of a Lattice Model for Proteins," *Proceedings of National Academy of Sciences* (1999).

D.A. Butts, M.B. Feller, C.J. Shatz, and D.S. Rokhsar, "Retinal Waves are Governed by Collective Network Properties" (submitted to *Journal of Neuroscience*).

V.S. Pande and D.S. Rokhsar, "High Temperature Unfolding Pathway of a Beta-Hairpin," *Proceedings of National Academy of Sciences* (submitted).

N. Putnam, V.S. Pande, and D.S. Rokhsar, "Nature of the Transition State for Protein Folding" (in preparation).

In vivo *Expansion of the Genetic Code*

Principal Investigator: Peter Schultz

Project No.: 98028

Project Description

The method of site-directed mutagenesis has greatly enhanced our ability to probe the relationship between protein structure and function as well as to engineer new proteins with altered properties. Recently, we developed an *in vitro* method that increases the number of amino acids that can be site-specifically incorporated into proteins beyond the 20 common amino acids. This method makes use of chemically aminoacylated suppressor tRNAs to deliver unnatural amino acids in response to a stop codon introduced site-specifically into the gene encoding the protein of interest. Amino acids with novel structural or electronic properties (including altered pK_as, nucleophilicities, backbone structures, and hydrogen-bonding properties) have been site-specifically incorporated into proteins to probe specific structural or functional questions. In addition, a variety of biophysical probes have been substituted into proteins using this technique. Although this methodology has significantly expanded our ability to chemically manipulate the structures of proteins, relatively small quantities of protein are produced and this method cannot be used to modify proteins *in vivo*. The aim of this project is to further develop the methodology to allow the site-specific incorporation of unnatural amino acids into proteins in living cells. The proposed work should significantly enhance our ability to make large quantities of proteins containing tailormade amino acids for (1) use in studies of protein structure and function (both *in vitro* and *in vivo*) and (2) specific bioengineering applications.

Accomplishments

Our overall strategy consists of four elements: (1) the design and synthesis of the unnatural amino acid; (2) the construction of an "orthogonal" amber suppressor tRNA (O-tRNA) that is not a substrate for any of the naturally occurring tRNA synthetases and that will eventually be used to deliver our unnatural amino acid in response to a UAG codon in the mRNA

encoding the protein of interest; (3) the selection of an aminoacyl tRNA synthetase (from a library of mutants) that recognizes the O-tRNACUA but does not recognize any endogenous tRNAs; and (4) the screening or selection of a library of mutants of this aminoacyl tRNA synthetase for the ability to acylate the O-tRNACUA with the unnatural amino acid but not a common amino acid. Initially, we will carry out experiments with *E. coli* because of the ease of genetic manipulations, high transformation efficiencies (essential in generating large libraries of mutants), and the availability of established screens and selections.

Starting with several structurally or biochemically characterized tRNA-aminoacyl tRNA-synthetase pairs (including the *E. coli* glutamine, yeast glutamine, yeast aspartate, and yeast tyrosine systems), we have rationally designed or imported from nature a total of four tRNAs that are orthogonal in *E. coli*. For an example, see Figure 1.

Using genetic selection, we have evolved mutant aminoacyl tRNA synthetases that charge these orthogonal tRNAs with natural amino acids. See Figure 2. Efforts are currently underway to use genetic selections as well as immunological screens to isolate mutant synthetase enzymes, which charge unnatural amino acids onto these orthogonal tRNAs. Generalizable positive and negative suppression selections have been developed toward the evolution of mutant yeast glutaminyl-tRNA synthetases that charge any of more than 100 unnatural amino acids with novel chemical or biophysical properties. Cell-surface screening systems are also being developed in which unnatural amino acids charged onto orthogonal tRNAs are displayed on the outside of *E. coli* and captured using monoclonal antibodies raised against a variety of target unnatural amino acids. Preliminary results from both these efforts are encouraging. Finally, we are expanding this approach toward generating tRNA-synthease pairs that use four-base codons.

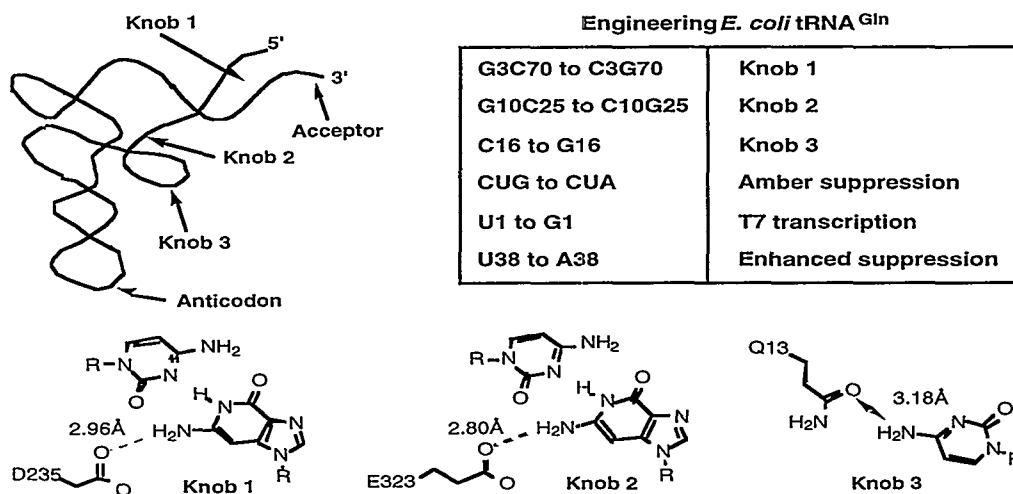| Engineering *E. coli* tRNA Gln	
G3C70 to C3G70	Knob 1
G10C25 to C10G25	Knob 2
C16 to G16	Knob 3
CUG to CUA	Amber suppression
U1 to G1	T7 transcription
U38 to A38	Enhanced suppression

Figure 1. Design of an orthogonal tRNA (O-tRNA) from E. coli tRNA$_2$^{Gln}.
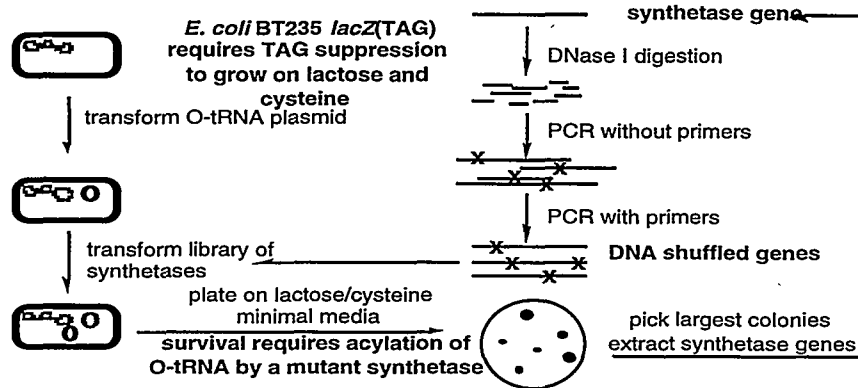
Figure 2. *Selection of a mutant glutamine aminoacyl-tRNA synthetase able to aminoacylate an orthogonal tRNA with glutamine.*

Protein Microcrystallization Robotic System

Principal Investigators: Joseph Jaklevic, Peter Schultz, Jian Jin, Bernard Santarsiero, and Raymond Stevens

Project No.: 98045

Project Description

It is well known that a major bottleneck for protein molecular structure determination using x-ray crystallography is the difficulty in producing quality crystals. Typically, to obtain a single, high-quality protein crystal, it is necessary to screen the protein sample against a multidimensional array of variables (e.g., reagents, salt concentrations, pH levels), or "mother liquids," comprising hundreds of crystallization trials. Done manually, these trials are so labor intensive and tedious that it is not practical to set up enough number of trials to ensure success. Another limiting factor is the scarcity of highly purified protein samples, with a typical current protein yield less than 1 ml. During conventional procedures, the amount of protein consumed per trail is ≈2 µl, thus limiting the total number of trials.

The development of the robotic systems for protein crystallization studies began in FY98. A robotic

system was conceptualized that automates the protein crystallization processes, synthesizes the necessary reagents, and optically screens the individual trials. The robotic system allows the user to vastly expand the number of possible reagents used to attempt crystallization. Compared to current state-of-the-art commercial systems, the first phase of this project will achieve an order of magnitude increase in throughput of crystallization trials. The second phase will explore the possibility of reducing the amount of protein sample used in a single trial to one tenth of a microliter to evaluate whether microcrystals can be grown with sufficient quality to determine the protein's structure.

The goal of the system is to generate and detect high-quality protein crystals. Every protein sample will first be screened against a coarse array of 480 standard mother liquids. An optical system will automatically monitor the individual trials for crystallization. As a crystal grows, repeated imaging will track its size, shape, and structure. If the crystal is of sufficient quality, the user will be alerted and the crystal removed for evaluation. If the crystal is suboptimal, two-dimensional arrays of new mother liquids will be automatically synthesized based on the identified mother liquid, and new crystallization trials will be created and monitored. Three discrete subsystems will perform the functions of (1) setting up a protein crystal growth plate, (2) optically monitoring the crystal growth trials, and (3) synthesizing the fine-grid screening reagents. Through the use of unique barcodes on each microtiter plate, a single database will be used to

communicate and store information among the three subsystems.

Accomplishments

Crystallization Subsystem

The crystallization subsystem is fundamental to the project because it is responsible for creating the crystallization screening trials. This complex subsystem requires multiple stations to store microtiter plates, grease the 48 individual wells per plate, add mother liquid to the wells, aspirate and dispense nanoliter volumes of protein and mother liquid, seal individual wells with cover slips, and store the completed plates. Expected throughput is one minute per row of eight wells, for a total of ten plates an hour and 3,840 individual trials in a single eight-hour shift.

Conceptual work began on the system in May and continued through August. Laboratory evaluation of commercial liquid handling systems in June led to the decision to purchase two BioJet systems from BioDot, Inc. to handle dispensing of the protein and mother liquid droplets. Work in June and July also included testing various mother liquids for physical characteristics and initial testing of prototype coverslip handling systems. The entire dispensing subsystem was assembled in September, with testing and software development conducted in October. Detailed drawings of all other system components were finished by early FY99 and sent for fabrication.

Optical Station

Because it can take from hours to months to grow a crystal, automatic monitoring of trials is necessary. To proceed with trials as quickly as possible, we are developing the optical system in two phases. The first stage consists of a commercial CrystalScore system from Diversified Scientific, Inc. to image and analyze crystal growth trials. Because this system does not have the automation or software capabilities necessary for the fully automated system, it will be used to evaluate the initial crystallization trials through the end of March 1999. The present work has consisted of decoding the CrystalScore database so that we can retrieve the scanned images, developing software to analyze these images using gradient-based image-processing techniques to flag crystals on the plate, and creating an Access database to store the images for user review. The same software will be utilized in the second phase, when an automated plate handling/imaging system will be developed to scan individual trials on any plate at a user-defined time interval.

Synthesizer

A commercial liquid handling system, Tecan Genesis RSP 2000, was purchased to handle the synthesizing of mother liquids for fine-grid screening. Approximately two months were spent writing software in Visual Basic (the common language across all three subsystems) to (1) provide a graphical means for referencing the microtiter plates and reservoirs on the Tecan deck, (2) test the liquid detection capability for various liquids and volumes, and (3) install and test the Toolbox subroutines for pipet translation and liquid handling functions.

Physics Division

Exploring Scientific-Computational Collaboration: NERSC and the Supernova Cosmology Project— Computational Innovations to Measure the Parameters of the Universe

Principal Investigators: Saul Perlmutter, Peter Nugent, Gerson Goldhaber, Donald Groom, and Gregory Aldering

Project No.: 96044

Project Description

In the next few years, we will measure the fundamental parameters of cosmology, using astrophysics techniques developed in the Supernova Cosmology Group. This project already requires unusual computational environments and capabilities. The future, larger amount of data will need innovations for near-real-time computation, fast access to large data sets, and tools for scientific visualization, networking, and "collaboratory" environments—all of which are research interests of NERSC. As a first step in a collaboratory, we are using T3E calculations to interpret our supernova spectra. We have also begun studies of image processing with supercomputers.

The key to successful cosmological measurements is to attack statistical and systematic error. This current project aims to reduce the systematic error associated with the minor variation in intrinsic brightness among Type supernovae (SNe Ia) by calibrating against features of the supernovae spectrum (spectral work that involves supercomputer simulations of supernovae atmospheres to produce "synthetic spectra"). This theoretical and phenomenological research will make it possible to prepare simulated spectra that will enable us to understand the distant supernova spectra and thus calibrate the supernova's brightness.

Accomplishments

Spectrum Synthesis on the T3E

Over the past four years, the Supernova Cosmology Project has discovered over 100 supernovae. Spectra for approximately 75 of these have been obtained at the Keck telescope, and 12 have been or are currently being observed by the Hubble Space Telescope. The major challenge for spectrum synthesis is to resolve any possible evolutionary effects in our high-redshift supernovae. Our highest redshift supernovae (SNe 1996cl, 1997ap, 1997ek, 1997en, 1997ez, and 1998bi [all with $z > 0.75$]) exploded when the universe was approximately one-half to two-thirds of its present age. The environment of the progenitors for these supernovae could be considerably different from the ones in which our nearby (calibrating) set of supernovae were formed. Current calculations running on NERSC's T3E and the IBM SP2 at the University of Oklahoma are attempting to capture the effects of metallicity in the progenitor system and mixing during the explosion as well as how both of these affect the resultant spectra.

Preliminary findings from this study can be found in Figure 1. Here we present a series of spectrum-synthesis models whose outer layers range in metallicity from one-tenth that of our solar
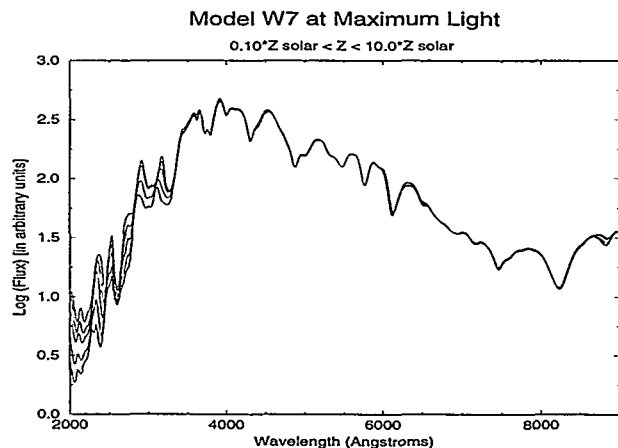

Figure 1. Maximum light models of a Type Ia supernovae with several different metallicities ($0.1 < z < 10.0$) in the outer 5,000 km/s of the atmosphere. Note that the differences in the spectra occur only in the far UV and that they are relatively minor.

neighborhood to ten times that amount. (The outer layers of the supernova are the only areas that contain remnants from the progenitor system; everything else is created during the thermonuclear explosion that marks the onset of the supernova.) Note that the only differences that occur are located in the very far ultraviolet (UV). Even with such a large change in metallicity, our findings show that there should be little effect on our measurements of the cosmological parameters, because the spectroscopic difference between these models are small and would influence only a handful of our highest redshifted supernovae.

We are also working on a method to determine the reddening due to interstellar dust (in either our own or the host galaxy) for a SN Ia. At 35 days after peak brightness, almost all SNe Ia have the same excess color, which is solely due to interstellar reddening. Through spectrum synthesis, we intend to test this hypothesis by examining the colors of a grid of models with a variety of initial conditions, chief among these being luminosity

Classification of Spectra

Following in the footsteps of P. Nugent and his collaborators, we have now confirmed and calibrated the relationship between the spectral ratios of several features seen in the spectra of SNe Ia and luminosity, using ≈20 recently obtained nearby supernovae spectra in the Hubble flow. In addition, the work of A. Riess has shown how the age of Type Ia supernovae (SNe Ia) can be determined to a surprising accuracy from a single spectrum. Nugent and Riess combined these methods to determine the peak luminosity of a SN Ia from a single spectrum found anywhere from two weeks before to two weeks after maximum light. These results are now being used as a check of our light-curve-based determination of the peak luminosity for our high-redshift supernovae and as a way of looking for possible evolutionary effects that might create a change in these relationships. Spectrum synthesis will be used to explain the reason behind these relationships in an effort to give them a more solid theoretical footing and allow interpolation between dates for which comparison spectra are not available.

Data Reduction

By taking advantage of the NERSC supercomputing facilities, we have greatly improved several data-reduction tasks. The two most important ones are k-corrections and fitting our data to various cosmological models.

K-corrections (placing the highly redshifted photometry on the same scale as nearby photometry through spectra) are best performed on a parallel supercomputer because they involve the processing and analysis of several hundred nearby spectra, each of which must be properly flux calibrated and redshifted, with its colors determined at every redshift where we have discovered a supernova. The results from this analysis are nearing completion, and a publication on this material is being prepared.

In addition to chi-square fitting to determine the cosmological parameters, we have also used bootstrap resampling of the data. We resample the data tens of thousands of times to determine the most likely fits to our parameters (the mass density of the universe and the vacuum energy density) as an independent check on the assigned error bars. A typical calculation can be completed in under an hour on 128 processors of the T3E. In the near future, we will begin to explore several new (and slightly unconventional) models of the universe using this procedure.

NERSC/Supernovae Cosmology Project Cooperative Efforts

As part of this NERSC-Astrophysics LDRD project, we have been working closely with NERSC staff to utilize the T3E for both spectrum synthesis and a future project aimed at using a massively parallel computer for image reduction. P. Tang (supported by partial LDRD funding in a joint NERSC/Supernova Cosmology Project collaboration) has been working with us in our effort to explore new methods in image reduction as well as how to implement these on a massively parallel machine like the T3E. He has so far created several of the fundamental building blocks for this analysis, including developing a set of matlab tools to perform image deblurring and denosing. Currently, he is working on selecting a suitable optimization algorithm and, after completion, its migration to the T3E.

Publications

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Fabrication of Charge-Coupled Devices on a High-Resistivity Substrate for Astronomical Imaging

Principal Investigators: Saul Perlmutter, Gerson Goldhaber, Donald Groom, Stephen Holland, Carl Pennypacker, and Richard Stover

Project No.: 97029

Project Description

Techniques developed at LBNL for central tracking applications in particle detectors are being applied to the design of charge-coupled devices (CCDs) for astronomical imaging. These will overcome present performance limitations as well as price and availability limitations. Having demonstrated imaging and high quantum efficiency with small test devices, we set as our most important goal the fabrication of a scientifically useful 2048 × 2048 pixel astronomical imaging device scaled up from the current prototype design. For the new technology to have its expected impact, it must be developed quickly.

In the course of detector research and development for the Superconducting Super Collider, a Physics Division group at LBNL developed a silicon device process that provided the first demonstration of monolithic integration of high-quality detector diodes with high-density, low-noise electronic circuitry, which is also compatible with conventional integrated circuits (IC) processes. The key is a highly efficient gettering process that actively removes detrimental impurities from the active volume. Present test structures have extended this method in two ways. On one side of a wafer, a fairly conventional CCD structure is fabricated. On the "back" side of the wafer is a window that also serves as an electrode during totally depleted operation. Imaging has now been demonstrated with small (200 × 200 pixel) test CCDs of this dramatically new design, and windows with superior properties have been produced. After thoroughly characterizing these structures, we will make a full-sized CCD.

Accomplishments

Progress on large area device fabrication was a key goal of the FY98 effort. A mask set containing CCDs varying in size from 512 × 512 to 2k × 2k was designed and procured. This set was the first to use the projection aligner donated by Intel Corporation. This aligner, which uses a scanning technique, removes the device size limitation imposed by the existing wafer stepper lithography tool.

Several wafers were processed through the entire ten mask fabrication procedure at the LBNL Microsystems Laboratory. A number of the plasma etch steps are performed at the University of California microfabrication facility. Preliminary test results verify successful fabrication, although more detailed testing on packaged devices is necessary to fully characterize the results of this fabrication run.

Fabrication of CCDs proceeded in parallel with other efforts, which included further characterization of the existing 200 × 200 prototypes and modeling of anti-reflection coatings.

The utility of the fully-depleted CCD for the detection of back-side near-IR emissions as a failure analysis tool for integrated circuits was demonstrated by our University of California Observatories/Lick Observatory collaborators. In addition, a 200 × 200 CCD was irradiated at the LBNL 88-inch cyclotron and characterized in terms of charge transfer inefficiency. Initial results confirm the expected improved radiation hardness of the technology.

The newly fabricated CCDs will use multi-layer antireflection coatings for improved quantum efficiency. An optical modeling framework that includes the effects of fringing has been developed. This framework was developed as an extension of earlier work at LBNL that treated the silicon substrate itself as a thin film, which is necessary to correctly

model the fringing. Multi-layer coatings can be included in the modeling, and preliminary designs have been generated for a two layer coating of indium tin oxide and silicon dioxide.

Publications

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Performance Modeling of Pixel and Silicon Strip Detectors for High-Luminosity Experiments

Principal Investigator: James Siegrist

Project No.: 97030

Project Description

Charged-particle tracking in high-luminosity experiments such as ATLAS depends heavily on measurements using pixel and silicon-strip detector devices. The U.S. ATLAS groups have been developing such detectors for use at high-rate hadron colliders, but many of the components still need research and development to provide a tracker designed to run for many years at a luminosity of $1034\ cm^{-2}\ sec^{-1}$. Survival at the high luminosities projected necessitates the use of pixels at radii below 30 cm. Strips must be placed at larger radii and must survive larger fluences than those foreseen for the silicon trackers designed for the Superconducting Super Collider.

This project seeks to concentrate on some outstanding simulation questions relating to silicon-tracker development, in both the pixel and silicon-strip systems. Not yet resolved, under the constraints noted above, are the chip testing specification simulation of signal development in radiation-damaged devices and characterization of the thermal behavior of these devices.

Accomplishments

Fabrication of a system purchased last year for module assembly and characterization was completed. Modules assembled using this new system underwent mechanical characterization.

Students supported by the LDRD Program worked on signal-simulation programs for the silicon detector. Figure 1 shows the signal development for electrons and holes computed for a simple pad geometry. This code was used by D. Nygren's x-ray group to look at position resolution on the x-ray conversion point within a silicon-strip detector. Both of these exercises resulted in a number of improvements to the code, which is now considered ready to use for silicon studies. Our new code supports full three-dimensional electric-field calculation for both pixel and silicon-strip geometries. The effect of the magnetic field on the motion of charge carriers in the silicon has been included. The new code supports a quasi-particle calculation of the drift, diffusion, and self-interactions of the electron and hole charge clouds.
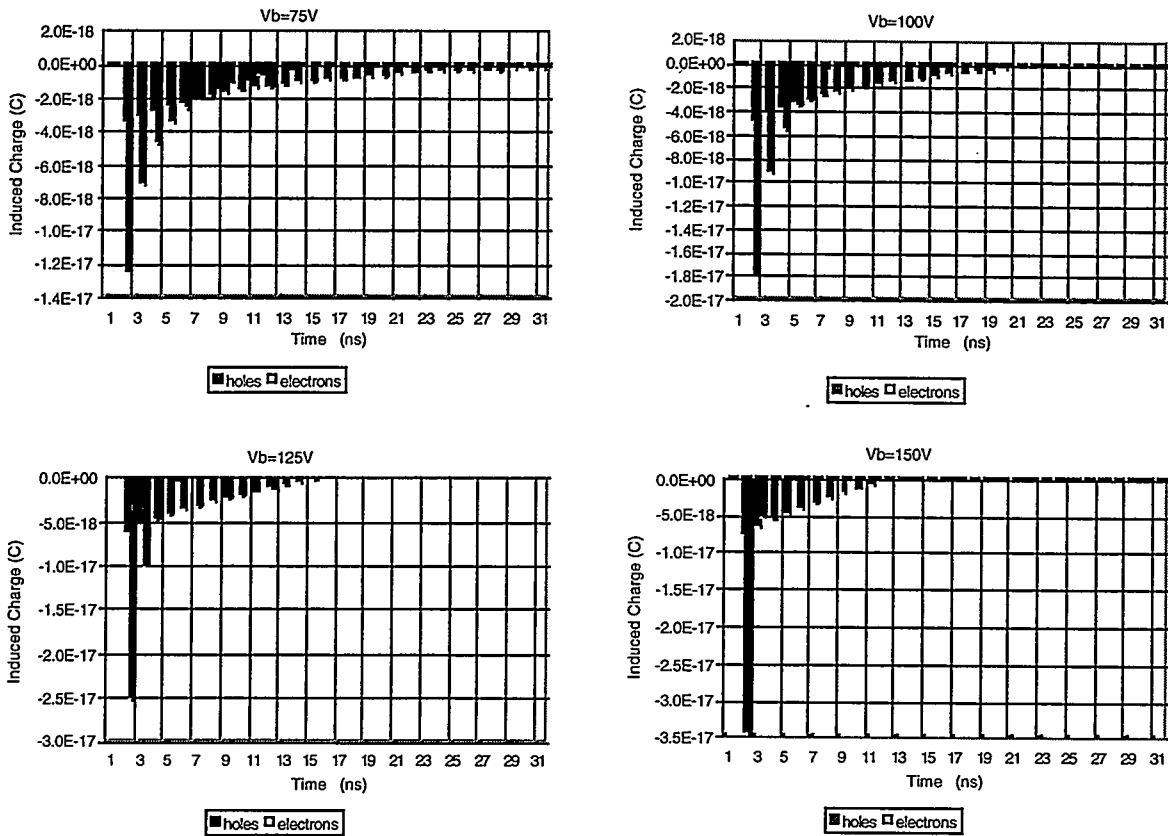
Figure 1. Signal development for electrons and holes computed for a simple pad geometry.

Cosmic Microwave Background Data Analysis

Principal Investigators: George Smoot, Julian Borrill, and Andrew Jaffe

Project No.: 97038

Project Description

The cosmic microwave background (CMB) is the universe's wallpaper. It is what is left over when all the radiation from astronomical objects is subtracted from what we observe. Theoretically, we understand it as the faintest echo of the Big Bang itself.

As the universe expands, the average energy of the matter and radiation drops. Today, it is three degrees above absolute zero, but 15 billion years ago—give or take five billion years—we think there was an arbitrarily hot Big Bang, when space and time came into being. Some 300,000 years later, the universe had cooled enough for the protons and electrons to stop bouncing off each other and electromagnetically couple to form neutral hydrogen atoms. In the absence of free electrons to scatter off, the photons simply continued in the direction they were last moving in until we detect them today. This collection of photons is what we call the Cosmic (because it fills the universe so completely and uniformly) Microwave (because of the frequency at which its spectrum peaks today) Background (because it originated further away from us than all other radiation we receive).

Despite its stunning uniformity—isotropic to a few parts in a million—it is the tiny perturbations in the CMB that contain its unprecedented view of the early universe. Already present before gravitationally bound objects had formed, these temperature differences are an imprint of the primordial density

fluctuations that seeded everything from planets to galaxy clusters and superclusters. As such, they promise to be an exceptionally powerful discriminant between competing cosmological models.

Subtracting the foregrounds from what we measure at a particular frequency is a difficult job, often requiring us to extrapolate from a source's intensity at its characteristic frequency to the microwave frequencies at which the CMB is measured. The observational equipment itself—mirror, detectors, and electronics—also introduces significant noise into our measurements, even when cooled to a few Kelvin. However, scanning each point in the sky many times allows us to distinguish between the signal and the noise components of the observations. Given a map of the sky temperature (Figure 1), and knowing something about the statistical properties of noise that went into it, we can now calculate the most likely underlying signal, and by how much it is the most likely.

Computing this maximum likelihood is now the limiting step in extracting cosmology from CMB observations. Recent successful flights of the MAXIMA and BOOMERanG balloon-borne detectors have produced the largest CMB datasets to date. Both experiments plan to fly again in 1999, to be followed by the MAP and Planck satellites in 2001 and 2007. Over that time, the maps produced will grow fro tens of thousands to millions of points, and the time the algorithms we currently use to analyze them will correspondingly increase from hours to millions of years (Table 1).

Accomplishments

In the first year of this project, we have developed a full-scale parallel implementation of the map-making and maximum-likelihood-analysis algorithms on the NERSC T3E. We are now using them to process data from the MAXIMA-1 and BOOMERanG North America flights, providing both insights into the cosmos and benchmark results against which to measure the performance of the new algorithms we are having to develop to process future datasets. The first maps from these first flights have been produced, and further analyses and results are under way.

Publications

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J. Borrill, "Power Spectrum Estimators For Large CMB Datasets," *Physical Review D* (in press) (1998) (astro-ph/9712121).

Figure 1. Map of imprint of universe's primordial perturbations in cosmic microwave background radiation.

Table 1. Computational resources required to analyze CMB datasets using the quadratic estimator algorithm, assuming 20 signal component and 5 iterations on (1) a single 250 Mz processor and (2) the indicated number of T3E nodes running at the equivalent of 600 MHz. For an N_p pixel map, the amount of RAM memory needed scales as N_p^2 and the number of floating point operations as N_p^3.

Dataset	Map Size	Computational Resources			
		Memory	Flops	Serial Time	T3E Time
BOOMERanG N. America	30,000	15 Gb	5×10^{15}	8 months	40 hours ($\times$ 64)
MAXIMA-1	40,000	25 Gb	10^{16}	16 months	40 hours ($\times$ 128)
MAXIMA-2	80,000	100 Gb	10^{17}	13 years	4 days ($\times$ 512)
BOOMERanG Antarctica	120,000	240 Gb	3×10^{17}	40 years	6 days ($\times$ 1024)
MAP	1,000,000	16 Tb	2×10^{20}	25 thousand years	
PLANCK	10,000,000	1600 Tb	2×10^{23}	25 million years	

Cross-Divisional

Research and Development for Kilometer-Scale Subsurface Neutrino Astrophysical Observatory

Principal Investigators: William Chinowsky, John Jacobsen, Douglas Lowder, Jozsef Ludvig, David Nygren, Gerald Przybylski, George Smoot, and Robert Stokstad

Project No.: 98029

Project Description

Detection of ultra-high-energy neutrinos of astrophysical origin is an unexplored frontier of great scientific interest to particle physics as well as astrophysics. At the highest energies observed (in cosmic rays), only neutrinos can traverse cosmological distances. Neutrinos can thus carry information about energetic processes and violent phenomena (e.g., active galactic nuclei) that occurred primarily in the early universe and are still not well understood. At these high energies, the interaction probability is sufficiently large that it is experimentally feasible to detect neutrinos with detectors at the kilometer scale.

The best methodology is a water Cerenkov technique, using arrays of large photomultiplier tubes in either deep ocean water or deep clear ice at the South Pole. Although each environment has its advantages and disadvantages, deployment techniques for ice are more mature. The design and realization of such a large detector present numerous technical and practical challenges. An innovative technical approach developed at LBNL and endorsed by both the Antarctic Muon And Neutrino Detector Array (AMANDA) (deep ice) and NESTOR (deep Mediterranean ocean) collaborations has now been partially realized, with important milestones on the horizon in the near future. In addition, LBNL (in alliance with NERSC) has made a large advance in the processing of the massive datasets generated by the AMANDA detector.

In summary, LBNL is preparing the technical pathways needed for a credible kilometer-scale detector proposal. Although the detector is likely to cost from $50–$100 million, the National Science Foundation (NSF) appears quite interested in this scientific direction and has encouraged us to submit a proposal to support construction of a test array for our kilometer-scale system.

Accomplishments

Development of Digital Test String

An improved application specific integrated circuit (ASIC), the analog transient waveform digitizer (ATWD), was developed, fabricated, and successfully tested. This new chip, which is at the heart of our digital system, combines the functions of analog wave form recording and the subsequent digitization of the analog information stored in each of the 128 cells forming a channel in the ATWD. This greatly increases the overall speed of the digital system. Based on this success, a larger number of chips was ordered for incorporation into the AMANDA digital string.

A new and comprehensive system design, tailored to operate in Antarctic ice, was presented to the community at a workshop in March 1998 that centered on ICEcube, the kilometer-scale detector planned for the South Pole.

The local-coincidence method to eliminate noise among the optical modules was studied in detail. Because the coincidence is taken at depth, the bandwidth requirements for the digital communications to surface are reduced significantly. Monte Carlo studies of the local-coincidence method were made and showed that, as well as reducing the amount of noise, this method improved the quality of the signal itself.

Members of the AMANDA collaboration interested in the digital approach endorsed the digital test string and agreed on a common approach and·subdivision of tasks. LBNL will develop the digital electronics for the optical module, and the Deutches Electronen Synchrotron Laboratory (DESY-Zeuthen) group will handle the surface data acquisition.

Engineering design of the prototype digital optical module (DOM) began, led by a newly recruited LBNL engineer. A proposal was prepared and submitted to the NSF for funds to purchase the hardware for the

digital test string. Presentations were made to the NSF in support of this proposal and approach to a kilometer-scale detector.

Digital System for Ocean Deployment

Many of the technical features of our digital system are useful for detectors operating in the ocean or ice (i.e., they are "phase neutral").

Development of a data acquisition system (DAQ) for NESTOR was begun, to be deployed in Mediterranean Ocean near the southwest corner of Greece. NESTOR's main scientific goals are the same as AMANDA's. When the conclusion was reached that the ATWD chip was working satisfactorily, effort began on a test system to gain experience with the ATWD in an actual working setting. Members of the NESTOR collaboration welcomed this effort because our test data acquisition system based on the ATWD will operate as a backup to the main NESTOR DAQ system, to be provided by a University of Rome group. Because technical problems have significantly delayed this latter system, the ATWD-based test system may ultimately serve an essential role in the NESTOR project.

The technical concept of the LBNL test DAQ for NESTOR incorporates programmable logic that may be downloaded after deployment from shore. This capability provides both safety against initial programming errors and flexibility for installation of optimized code at will. In addition, the logical organization of the LBNL test DAQ permits geometry-sensitive majority logic for maximal retention of true muon signals, with efficient rejection of backgrounds. The net result is a reduction of noise transmission by roughly a factor of 1000. By utilizing real-time coincidence techniques in this manner, we similarly reduce the burden of on-shore data reduction and analysis.

Significant portions of the design and prototyping were completed. The test DAQ for NESTOR could not be completed before efforts were switched to the AMANDA test string design. The electronic design is nearly complete: two of the three circuit board layouts are finished, and the third is almost done. Most of the software, however, still needs to be coded. Much of the design effort for NESTOR also applies to AMANDA. Until the AMANDA test string design is complete and construction is proceeding on schedule, only minimal efforts can be made on our test DAQ for NESTOR.

Simulations and Data Processing

In collaboration with NERSC, we made progress on techniques to process and analyze the massive amounts of data generated by the current AMANDA detector operating at the South Pole. This massive data set exceeds the analytical capacity at the current AMANDA collaboration. LBNL and NERSC received, stored, and filtered all the data from the 1997 campaign and are doing the same for the 1998 data. Simulation and data analysis codes were obtained and ported to LBNL computers. The LBNL group is developing concepts and procedures that will be necessary as the data-generation capacity increases with detector size.

Specifically, the local-coincidence method was studied for both a hardware trigger and software filter by using Monte Carlo simulations and actual data from AMANDA.

Physics and Biology of Boron Neutron Capture Therapy

Principal Investigators: Eleanor Blakely, Thomas Budinger, and William Chu

Project No.: 96002

Project Description

Glioblastoma multiforme is a cancer of the brain, known for the manner in which the cancer cells extend their tendrils into surrounding healthy brain tissue. The disease is virtually inoperable, resistant to conventional radiation therapies, and always fatal, usually within six months of onset. Each year, glioblastoma multiforme kills approximately 15,000 people in the United States.

Boron Neutron Capture Therapy (BNCT) is a potential treatment procedure. BNCT uses neutron absorption in a boron nucleus to create a localized radiation that would, we hope, be highly selective in killing the cancer cells wherever they are located in the brain.

The research into BNCT supported by this project is represented by three subprojects: "The Influence of Microenvironmental Factors on the Uptake and

Cytotoxicity of Boronated Protoporphyrin (BOPP)," "*In Vivo* Kinetics and Distribution of BNCT Compounds," and "Measurement of Low-Energy Neutron Production Using a Be Target."

Subproject 1: The Influence of Microenvironmental Factors on the Uptake and Cytotoxicity of Boronated Protoporphyrin (BOPP)

Eleanor Blakely, Lenka Maletinska, Kathleen Bjornstad, and Trudy Forte (LBNL), and Dennis Deen (UC San Francisco)

Subproject 1 proposes to extend our pre-clinical investigations of human glioblastoma multiforme tumor-cell biology in order to enhance our drug design for BNCT. We have been studying the pharmacokinetics and toxicity of BOPP, which received USFDA approval for an Investigational New Drug (IND) application in May 1998, and which may be a candidate pharmaceutical for BNCT. The drug has been in clinical trials for use with photodynamic therapy (PDT) of human brain tumors at the Royal Melbourne Hospital in Melbourne, Australia, since June 1998. To date, 14 patients have been entered in the Phase 1 dose-escalation trial with no evidence of any toxicities. Porphyrins are known to associate with plasma lipoproteins (particularly low-density lipoproteins [LDLs]) and are thus likely to be taken up into cells by the high-affinity, saturable LDL receptor mechanism. We showed last year that BOPP is incorporated into the human glioblastoma cell line SF 767 and requires the presence of lipoproteins for maximum uptake into cells. We concluded from these studies that, like other porphyrins, BOPP forms a complex with LDL before it is taken up into the SF 767 cells via the LDL receptor. We also obtained preliminary new evidence for significant numbers of saturable LDL receptors on SF 767 cells. During the past year, we set out (1) to determine quantitatively the LDL receptor numbers present on actively dividing SF 767 cells and (2) to screen other glioma lines from biopsy material from the UCSF Brain Tumor Research Center.

Accomplishments

Classical LDL binding studies were carried out at 4°C with ^{125}I-LDL in the presence and absence of a five-fold excess of unlabeled LDL. The latter provides information on the nonspecific binding of LDL. To ensure that LDL receptors were maximally up-regulated, the cells were grown for 24 hours in a medium containing lipoprotein-deficient serum. The difference between total ^{125}I-LDL binding and nonspecific binding provides information on the saturable, specific binding of LDL. LDLs were labeled by the Iodo-Bead method of Pierce (Rockford, IL). Binding curves from four replicate experiments clearly demonstrated a saturable and specific binding component where saturation occurred at approximately 760 ng ^{125}I-LDL/mg cell protein. A Scatchard plot analysis indicated high affinity binding of LDL to its receptor, where the K_d (binding affinity) was 4.9 nM. From these data, we calculated that approximately 210,000 receptors per cell exist at 4°C. To place this receptor data in perspective with receptor number on other cell types, we have compared the K_d and B_{max} (maximal LDL binding) data available in the literature with several other human cell types. This information suggests that, compared to fibroblasts and the human hepatoma line (HepG2), SF 767 cells have a greater B_{max}; however, K_d is similar for fibroblasts and SF 767 cells, and this affinity is greater than that found in HepG2 cells. Overall, the data suggest that the SF 767 glioblastoma cell line has large numbers of LDL receptors that provide a potential mechanism for targeting therapeutic agents to these cells. An additional five other human glioma cell lines (U251, SF 763, A172, U87MG, and U343) have been screened with this assay. The receptor numbers show considerable heterogeneity between the different glioma lines, but may indicate a potential method to screen biopsy material for appropriateness of porphyrin compounds in BNCT for individual glioblastoma tumors.

Subproject 2: *In Vivo* Kinetics and Distribution of BNCT Compounds

Thomas Budinger and Scott Taylor

The goals for the Center for Functional Imaging's involvement in LBNL's BNCT project (Subproject 2) are (1) to provide a noninvasive method to determine the spatial and temporal distribution of boron-porphyrin complexes in tumors and other tissues, (2) to develop new and unique compounds to increase boron deposition in tumors, (3) to assist in the selection of the appropriate compounds for BNCT, and (4) to develop clinical strategies to maximize the boron uptake in the individual patient.

The third goal has been expanded to involve the development of isotopes and radiolabeling techniques to provide for the general use of non-invasive imaging for any and all boronated compounds

currently under development throughout the world. This activity will require the development of targets for the production of longer-lived positron-emitting isotopes on the Center's biomedical cyclotron (e.g., ^{55}Co, ^{76}Br, ^{124}I). Synthetic techniques must also be established to use these isotopes for radiolabeling the carborane (carbon/boron) complexes used by most BNCT agents as the boron delivery moiety.

Accomplishments

The FY98 support was used to complete Goal 1 and for initiating studies in Goals 2 and 3 to provide preliminary results.

The use of positron-emission tomography to follow boronated porphyrin kinetics and distribution was successfully accomplished in animal models with a BOPP currently under study at UCSF. BOPP was successfully radiolabeled with radioisotopes of copper (^{64}Cu and ^{67}Cu) and was used to examine *in vivo* distribution in tumor-bearing rats and in normal and atherosclerotic rabbits. The Cu-BOPP was found to accumulate in tumors and clear blood at rates comparable to unlabeled BOPP, and dosimetry results indicated that ^{64}Cu-labeled porphyrins could be utilized in humans to study these potential BNCT-agents.

This first set of a new class of BNCT agents is also near the end of production. Certain polyamines known to have a high tumor uptake with low cytotoxicity have been prepared in our laboratory and sent to our collaborators at UCLA for the attachment of carborane complexes.

Once boronated, these agents will be used for radiochemistry studies at LBNL to establish the procedures for the covalent halogenation (radioisotopes of F, Br, I) of the molecule's carborane portion or for the chelation of Co radioisotopes between two carboranes in a tethered-dicarborane complex. They will also be subjected to a battery of cell-culture and animal-model studies to determine their ability to selectively deliver large amounts of boron to tumor cells. The carborane complexes have already been prepared for us by M.F. Hawthorne and his co-workers in the Department of Chemistry at UCLA. Initial experiments to develop the radiochemistry methods have already been carried out. This methodology should prove adaptable for use in the radiolabeling of any BNCT agent.

Subproject 3: Measurement of Low-Energy Neutron Production Using a Be Target

Luc Béaulieu, Larry Phair, Gordon Wozniak, and Luciano Moretto (Nuclear Science Division)

William Chu and Bernhard Ludewigt (Life Sciences Division)

Nicola Colonna (INFE, Bari, Italy)

The most useful neutrons for BNCT are epithermal neurons with energy falling between 1 keV and 20 keV. High-energy (100 keV to several MeV) neutrons produced in nuclear reactions must be moderated to the clinically useful epithermal energy. The lower the primary neutron energies, the more readily the neutron energy can be moderated. In Subproject 3, we have explored the possibilities of producing lower-energy neutrons by measuring the low-energy (<200 keV) neutron spectrum produced in (d,n) reactions on several target materials at a deuteron energy slightly above 1 MeV.

Our approach proposed in the BNCT field task proposal (FTP) is to generate epithermal neutrons by moderating the neutrons (200–800 keV) produced in the ^{7}Li(p,n) reaction. In this approach, a beam of 2.3-MeV protons at a current ~50 mA dc results in a heat load greater than 100 kW to the lithium target. This approach presents several challenging problems, and finding technical solutions (such as designing a high-current power supply for the electrostatic quadrupole (ESQ) accelerator, developing a target design, and moderating neutron energies) constitutes the main research effort of the FTP. Although we have already developed good solutions to these problems, we want to closely examine alternative materials, such as beryllium or carbon, as possibly better neutron-production solutions for a hospital-based BNCT facility.

Accomplishments

The experiments were performed at the LBNL 88-Inch Cyclotron, using deuteron beams of ~1.5 MeV and proton beams of ~2.5 MeV. The neutron-production reactions investigated were ^{9}Be(d,n)^{10}B at a deuteron energy slightly above 1 MeV, and ^{12}C(d,n)^{13}N and ^{13}C(d,n)^{14}N reactions at a deuteron energy of ~1.5 MeV.

Our experimental results indicate that, among the different reactions, only ^{12}C(d,n)^{13}N and the

$^9Be(d,n)^9B$ reactions at an energy of proton <3 MeV present a spectral purity of low-energy neutrons comparable to the $^7Le(p,n)$ reaction. Their yield seems too low, however, for currently attainable accelerator technology. On the other hand, both the $^9Be(d,n)^{10}B$ and $^{13}C(d,n)^{14}N$ reactions present reasonably high yields but are affected by sizable contamination of high-energy neutrons. Although neutrons of several MeV energy are emitted in the $^9Be(d,n)^{10}B$ reaction, most of the contamination for the ^{13}C targets is concentrated at neutron energies slightly above 1 MeV, so that the quality of the epithermal neutron beam may not be significantly worsened by the presence of this higher energy peak.

In conclusion, the low-energy (d,n) reactions investigated produce neutrons with lower yields and, in most cases, higher average energy than the $^7Li(p,n)$ reaction at a proton energy of 2.5 MeV. Our results suggest, however, that a more cost-effective accelerator facility might result from the use of the $^{13}C(d,n)^{14}N$ reaction, with a proper choice of the deuteron energy and moderator design. In our opinion, this reaction represents the only potentially interesting alternative for neutron production for BNCT among the different (d,n) reactions studied so far. More accurate measurements and detailed simulations of the moderation to produce the flux of epithermal neutrons will be necessary for the therapy.

Because of the limited resolution for high-energy neutrons and the uncertainty on the absolute yield, the present results are by no means conclusive. They are meant to stimulate further discussion and measurements necessary to identify any proton- or deuteron-induced reactions that would lead to simple and inexpensive accelerator-based neutron sources, while satisfying all of the dose requirements for BNCT.

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High-Fidelity Simulation of Diesel Combustion

Principal Investigators: Philip Colella, Nancy Brown, and Michael Frenklach

Project No.: 96029

Project Description

The goal of this project is to develop a three-dimensional modeling capability for diesel combustion to fill a critical need for high-fidelity simulations in support of engine design. Our approach is based on the development of high-resolution adaptive algorithms for three-dimensional fluid dynamics in complex geometries, combined with a representation for turbulent combustion based on a partial perfectly-stirred reactor model that can represent complex chemical kinetics appropriate to diesel combustion and mechanisms for the production of soot.

The first major area of our research has focused on the development of suitable extensions to complex boundary geometries arising in diesel engine applications of the high-resolution and adaptive finite difference methodology. This methodology was developed by investigators in the Computing Sciences Division for low-Mach-number reacting flows. Our approach is based on a Cartesian mesh embedded boundary representation of the boundary geometry, in which complex geometries are represented on a rectangular grid on which the region containing the boundary has been cut away. This approach has the capability of representing highly complex geometries

arising in engineering applications such as diesel engines.

The second major area of our research has focused on building a chemical mechanism that includes a robust description of hydrocarbon oxidation and soot formation.

Accomplishments

Embedded Boundary Methods for Partial Differential Equations

During FY97, we developed an easily used software infrastructure for Cartesian mesh embedded boundary methods, based on a graph-theoretical description. In this approach, we generalized the notion of a rectangular grid index space to the abstract graph of an embedded boundary described above. Arrays were then defined on subsets of the index space, analogous to the definition of ordinary multidimensional arrays indexed by subsets of the rectangular lattice. During FY98, we used this infrastructure to develop a number of important capabilities that are critical for the development of computational fluid dynamics algorithms for diesel combustion.

We developed a number of numerical algorithms for partial differential equations (PDEs) in three space dimensions, including adaptive mesh versions of the embedded boundary methods for hyperbolic PDEs such as those that arise in the advective transport of fluids as well as elliptic and parabolic solvers on a single grid. We also implemented a prototype single-grid version of a time-dependent incompressible flow solver, a key milestone for computing the low-Mach-number flows arising in this application. We also used these algorithms as a test bed for performance tuning of the underlying software infrastructure, reducing the overhead of using these high-level abstractions by as much as two orders of magnitude, so that the overhead became a small fraction of the total computational cost. Finally, we developed tools to translate surface triangulations of engineering geometries derived from Computer-Aided Design (CAD) descriptions to descriptions based on our infrastructure. This was done by using Cart3D, a tool developed by NASA Ames and the Courant Institute, which takes surface triangulations as input and produces as output a Cartesian grid description that is mathematically equivalent to our own. We developed a translator from their data representation to ours and demonstrated its use on a cylinder and port geometry obtained from Caterpillar, Inc.

Chemical Mechanisms for Hydrocarbon Oxidation and Soot Formation

The primary focus of our FY98 work in this area was on the study of polycyclic aromatic hydrocarbons (PAH), which have been identified as carcinogenic products of combustion and precursors for soot particle nucleation. The desire to minimize these negative environmental consequences leads to the study of PAH growth. For fuels without aromatic content, aromatic species must form through a process in which successive hydrocarbon molecules combine, eventually forming five- or six-member rings. We studied the formation of PAHs with up to four six-member rings by initiating detailed kinetic modeling of PAH in ethene diffusion flames and then comparing our modeling results with measured species profiles of Olten and Senkan.

The operating parameters of the flame were (1) a fuel stream with 75% C_2H_4, 25% Ar, and a velocity of 13.16 cm/s; (2) an oxidizer stream with 25% O_2, 75% Ar, and a velocity of 16.12 cm/s; (3) a nominal strain rate of 24 s^{-1}; and (4) plug flow boundary conditions. The Wang and Frenklach mechanism developed to model PAHs in premixed flames was initially used and later modified to add a number of reactions to produce C_3H_5 and C_3H_6, leading to C_3H_4 and increasing the rates of production of C_3H_3 from C_2H_2 and single ring compounds from C_3H_3. A number of other reactions were also added to improve our descriptions of one-, two-, and three-member ring compounds that serve as soot precursors. The

formation of benzene (A1) was modeled using an irreversible combination of propargyl (C_3H_3) and the reversible addition of acetylene to C_4Hi. Growth of aromatic species through napthalene and phenanthrene to pyrene was modeled using the hydrogen abstraction, acetylene addition (HACA) mechanisms. Figure 1 shows the comparison between measured and computed radical species as a function of distance. Measured and calculated radical species profiles compare very well for the indicated species. Our new mechanism is also able to predict aromatic levels in good agreement with measured values.

Predictions were compared with experiments in a sooting flame, and the sensitivity of the predictions to experimental uncertainties was considered. We found by this comparison with experiment that predictions are especially sensitive to uncertainties in probe placement, radiation heat losses, and possible O_2 leakage to the fuel stream. Aromatic species predictions were found to have high sensitivities to all three.

We experienced problems in matching measurements of C_3H_4 and CH_4 and were not able to find a reasonable set of rates to match the experimental results. The CH_4 profile was mainly determined by the equilibrium between CHi species but may also be influenced by low temperature oxidation chemistry. Predictions of linear hydrocarbons with even numbers of C atoms are in agreement with measurements, while those with odd numbers of C atoms are generally underpredicted. A paper
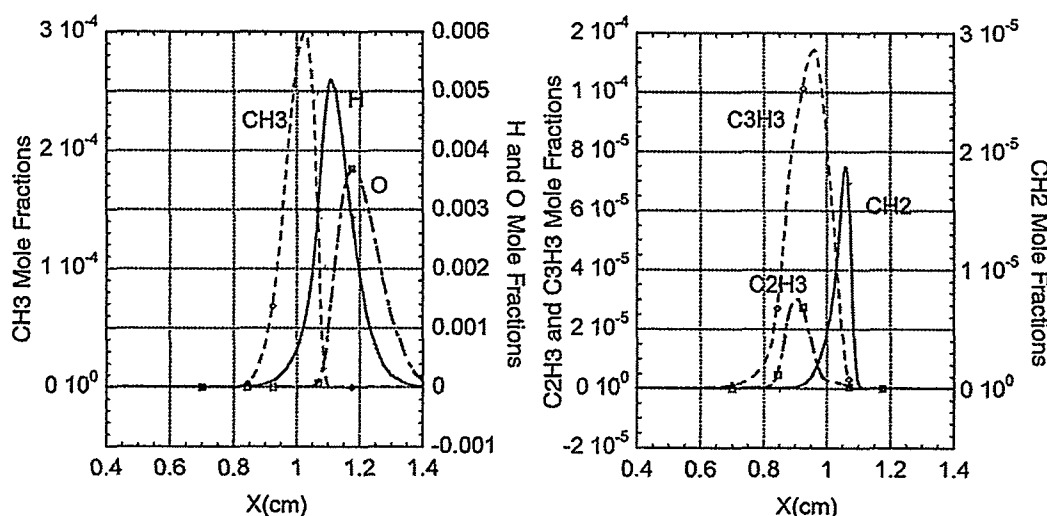

Figure 1. Radical species concentrations (mole fraction) as a function of distance (cm). Symbols are measurements; lines are predictions. X is the distance in centimeters measured from the fuel nozzle.

describing this research will be submitted for publication.

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VUV/Soft X-Ray Synchrotron Radiation Research for Molecular Environmental Science

Principal Investigators: David Shuh, Neville Smith, Tetsu Tokunaga, Geraldine Lamble, Satish Myneni, and Glenn Waychunas

Project No.: 98030

Project Description

Molecular environmental science (MES) has emerged in the last few years in response to the need for basic research to underpin long-term solutions to environmental problems. The objectives of MES research are to provide information on the chemical and physical forms (speciation), spatial distribution, and reactivity of contaminants in natural materials

and man-made waste forms; and to develop a fundamental understanding of the molecular-scale environmental processes, both chemical and biological, that affect the stability, transformations, mobility, and toxicity of contaminant species. Chemical reactions at the surface of natural solids play dominant roles in many environmental processes. Consequently, molecular-level studies of contaminant reactions at interfaces are an important focus of MES research. The vacuum ultraviolet (VUV)/soft x-ray synchrotron radiation (SR) region has traditionally been one of the domains of surface-science research. However, experimental MES studies in this spectral region are complicated by the need for *in-situ* studies with aqueous solutions, spatial and spectral resolution, and the ability to characterize the speciation of contaminants at very low concentrations. The combination of new technologies provided by third-generation, high-brightness SR sources, improved vacuum techniques, and improved detectors provides the opportunity for new applications of traditional VUV/soft x-ray surface-science methods to MES issues.

Fundamental studies of several specific issues in molecular environmental science have been initiated by techniques unique to the VUV/soft x-ray region. Well-developed techniques in the VUV/soft x-ray energy region have distinct advantages in surface sensitivity, spectral resolution, and spatial resolution when compared to techniques used for MES research in the x-ray region. Our focus will be on fundamental spectroscopy/microscopy investigations of contaminant speciation in wet and model environmental systems at mineral interfaces, with organic materials, microorganisms, and solid-state materials. This activity will include several key species containing C, N, Cr, Tc, Se, Mn, and selected actinides to provide molecular-level information to explain macroscopic behavior. This coordinated environmental research effort utilizes the K-edges of the light elements, L-edges of the transition metals, M-edges of the actinides, and low-lying core levels of other elements to obtain comprehensive chemical information. Many of these core-level thresholds are exclusive to the VUV/soft x-ray spectral region and are optimal for investigation at the Advanced Light Source (ALS). The experimental studies will be complemented by a theoretical component extending existing spectral modeling into the VUV/soft x-ray region and will provide valuable data for computational efforts. Additionally, this research effort will develop specialized VUV/soft x-ray SR experimental instrumentation necessary for MES

research. This research program will demonstrate the utility of VUV/soft x-ray SR methodologies for the investigation of a range of MES issues.

The MES research activities are a collaborative and multidisciplinary approach to utilizing VUV/soft x-ray SR techniques for MES research, involving scientists of the Advanced Light Source Division, Chemical Sciences Division, Earth Sciences Division, and outside participants. The initial studies will make use of existing endstations, beamlines, and available beamtime at the ALS while specialized instrumentation needed for future MES studies is developed.

Accomplishments

Initial studies of hexavalent chromium (Cr(VI)) reactions with different species of microorganisms have been performed with *Bacillus subtilis* and its spores, *Escherichia coli*, and an unnamed OYS3 species that was isolated from a U.S. DOE site. The preliminary studies indicate that Cr adsorbs at the microorganism-solution interfaces within minutes after Cr(VI) solutions were added to microorganism cultures (Figure 1, left panel). Detailed near-edge x-ray absorption fine structure (XAFS) studies have determined that the surface-reacted Cr was in the nontoxic Cr(III) form (Figure 1, right panel). Further Cr(VI) reduction was found only at the interfaces and not in the aqueous solutions. These studies

demonstrate that site-specific information on contaminant transformation can be obtained using soft x-ray microscopy and spectroscopy techniques.

The combination of x-ray fluorescence microprobe (XRFM) and micro x-ray absorption fine structure (μ-XAFS) techniques has been implemented over the past year at the ALS. These techniques are powerful methods for investigating a range of scientific issues pertinent to earth and environmental science. Recent spatially resolved heavy metal studies have examined the kinetics of sorption on clay surfaces, uptake in plants, and the symbiosis between fungi and higher plants with regard to uptake (see Publications). Figure 2 shows the elemental maps and spectra from the zinc-containing fungi study. These results suggest that Zn oxalate is important in the mechanism of contaminant uptake, retention, or conversion in its symbiosis with higher plants. Micro-XAFS data has been collected, in several cases, into the extended-XAFS region, where full structural analysis is possible. XAFS calculations are underway, simulating both the near edge and the extended-XAFS data.

X-ray emission spectroscopy (XES) shows promise for MES studies because it is applicable to "wet" or other intractable environments such as those accompanying radioactive materials. However, there is a lack of fundamental knowledge about the XES responses from species of environmental importance. XES and near-edge XAFS spectra have been obtained at the
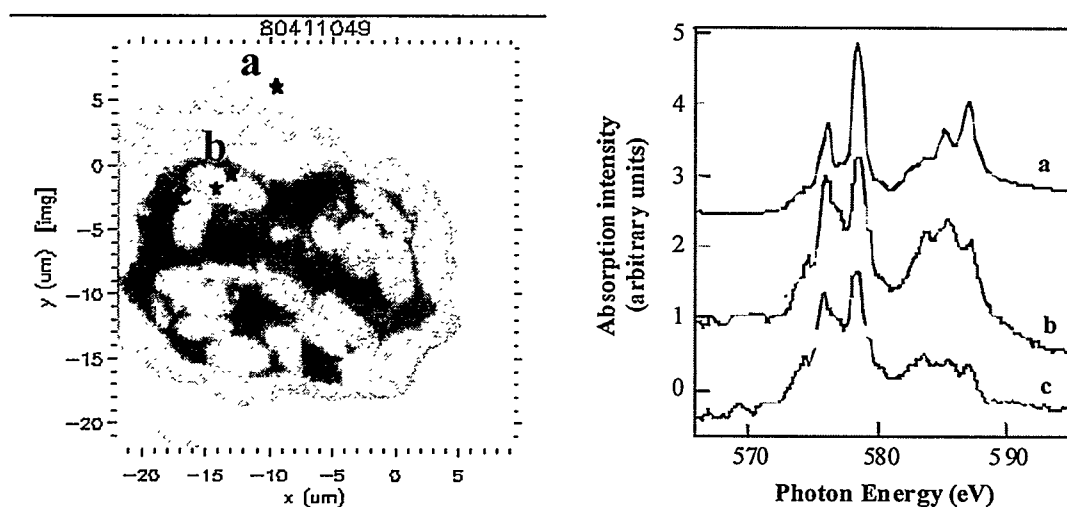

Figure 1. Scanning transmission x-ray microscope image of OYS3 species at Cr-edge (left), and L-edge spectra of Cr from Cr(VI) solution (a), microorganism-solution interface (b), and interior of microorganism (c) [right]. The identification of the microorganism species is currently underway.
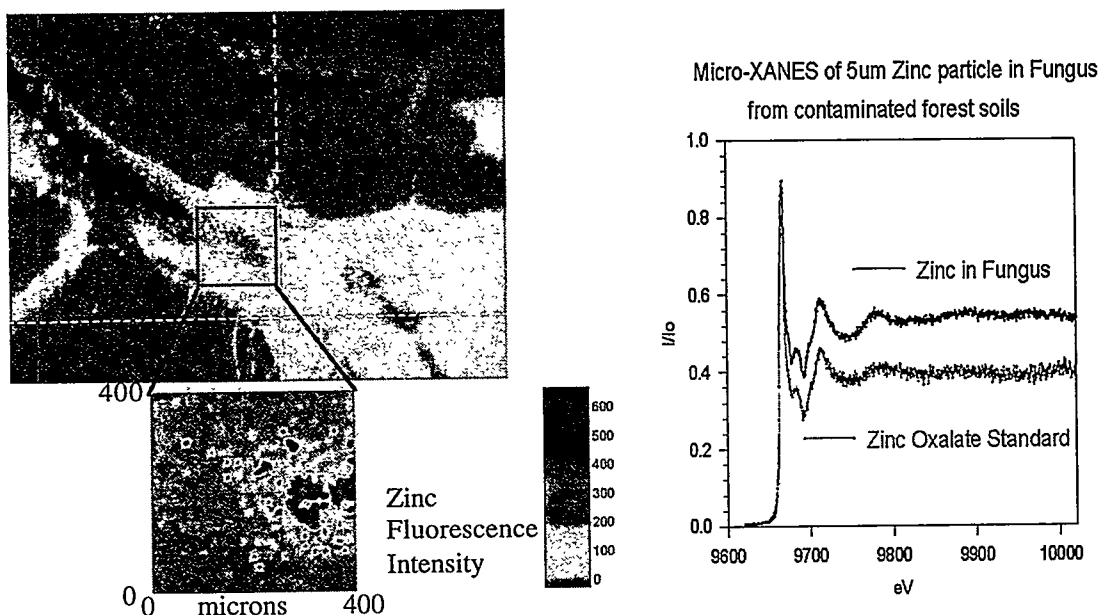
Figure 2. Optical micrograph of fungi in its natural state (top left) with a Zn elemental fluorescence map (lower left). XAFS spectra at Zn K edge from a fungus area with a high concentration of Zn particles and a Zn oxalate standard.

uranium 5d edge from a series of uranium oxides UO_2, U_3O_8, and UO_3 as a prerequisite to studies of actinides in real environmental materials. Representative XES and XAFS spectra from UO_2 are shown in Figure 3. The results from the uranium oxide series clearly distinguish the various oxides from one another and form the basis for actinide investigations to follow. Combined XES/XAFS

investigations have also examined novel C thin films designed to sorb metals and have characterized the speciation of several nonradioactive metal ions waste form glasses.

The ALS evaluation of the viability of low-energy grazing-incidence x-ray-absorption spectroscopy (GIXAS) techniques and methodology for
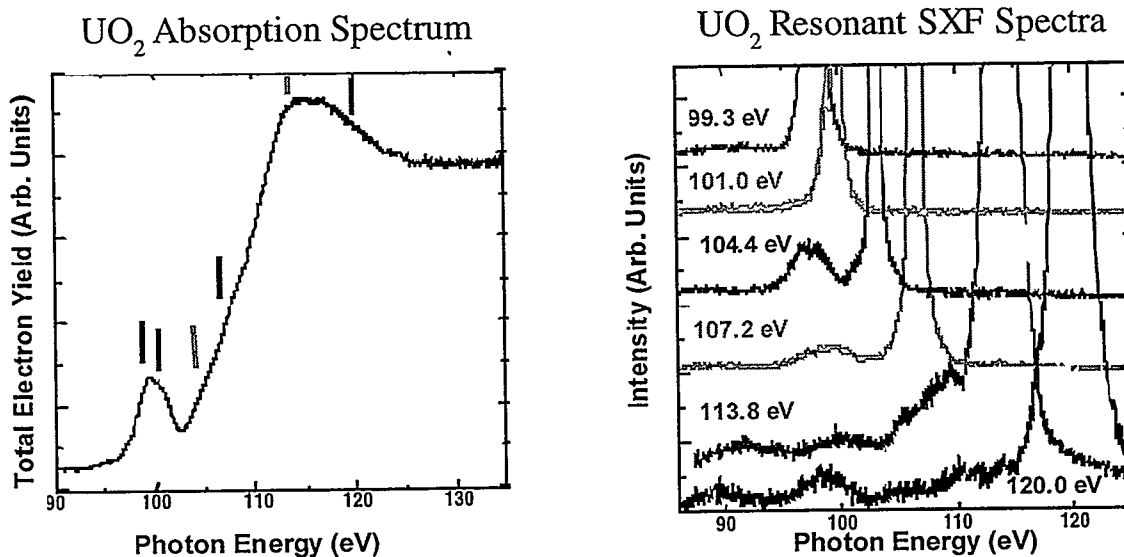

Figure 3. Uranium dioxide near-edge XAFS spectrum (left) and corresponding soft x-ray emission spectroscopy spectra (right) collected at energies corresponding to features indicated in XAFS spectrum.

applications in the 1–4 keV range is proceeding. The theoretical calculations of grazing-incidence angles and reflectivity profiles have begun for model systems. Experimental work that builds on the theoretical calculations is in the design stage. The initial calculations show that lower-energy GIXAS methods are less sensitive to surface roughness, and are practical above about 2 keV. The increased signal/noise with GIXAS techniques allows for much-improved sensitivity for surface sorption and precipitation characterization over what would ordinarily be possible at the P, S, Cl, and K edges.

Higher-energy GIXAS experimental studies continue to investigate iron-oxide formation on quartz surfaces. The purpose of this study is to determine the formation mode of ultrathin iron-aluminum oxide coatings on quartz and silicates in nature, its transformation, and sorption properties. Past bulk studies have shown that surface coatings usually dominate the sorption characteristics of soil and sediment-silicate grains.

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Acronyms and Abbreviations

ACPI	Accelerated Climate Prediction Initiative
AFM	atomic force microscopy
ALS	Advanced Light Source
API	application programming interface
ARIM	ALS-Accelerator and Reactor Improvement Modification
BaBar	B/B-bar (system of mesons produced at SLAC)
BCS	Bardeen-Cooper-Schrieffer
BEARS	Berkeley Experiments with Accelerated Radioactive Species
BES	Basic Energy Sciences
BGO	Bismuth-Germanate
BIF	Biomedical Isotope Facility
BNCT	Boron Neutron Capture Therapy
BNL	Brookhaven National Laboratory
BOPP	boronated protoporphyrin
CAC	chromatin assembly complex
CAF-1	chromatin assembly factor-I
CAFE	corporate average fuel economy
CCD	charge-coupled device
CCSE	Center for Computational Science and Engineering
CDF	Collider Detector at Fermi Laboratory
CE	capillary electrophoresis
CERN	European Organization for Nuclear Research
CERTS	Consortium for Electric Reliability Technology Solutions
CMB	cosmic microwave background
CMR	colossal magnetoresistance
COMPS	cluster of multi-processor systems
COS	class of service
DAC	diamond anvil cell
DM	density matrix

DPSS	Distributed-Parallel Storage System
DSWA	Defense Special Weapons Agency
ECL	electrochemiluminescence
ECR	electron cyclotron resonance
EDTA	ethylenediaminetetra acetic acid
EECS	Electrical Engineering and Computing Sciences (UCB)
EETD	Environmental Energy Technology Division
EM	electron microscopy
EMSA	electrophoretic mobility shift assays
ER-LTR	DOE Energy Research–Laboratory Technology Research
ERG	Energy Renormalization Group
ESQ	electrostatic quadrupole
EXAFS	extended x-ray absorption fine structure
FAA	Federal Aviation Administration
FAME	fatty acid methylester analysis
FEL	free-electron-laser
FERC	Federal Energy Regulatory Commission
FESEM	Field Emission Scanning Electron Microscopy
FGs	ferrofluids for guiding liquids
FIB	focused ion beam
FISH	fluorescence *in-situ* hybridization
FRET	fluorescence-resonance-energy transfer
fs	femtosecond
FTP	field task proposal *or* file transfer protocol
FTs	ferrofluids for tracing liquids
GIXAS	grazing-incidence x-ray-absorption spectroscopy
GMR	giant magnetoresistance
HACA	hydrogen abstraction, acetylene addition
HENP	High Energy and Nuclear Physics
HERS	high-energy-resolution spectrometer

HHMI	Howard Hughes Medical Institute	MEXH	multi-energy x-ray holography
HiPPI	high performance parallel interface	MICS	Mathematical, Information, and Computational Sciences Division
HMM	hidden Markov model		
HPSS	High Performance Storage System	μ-XAFS	micro x-ray absorption fine structure
HTS	high-temperature superconducting	MIDI	microbial identification system
I/O	input/output	MINC	multiple interacting continua
IC	integrated circuit	MPI	message passage interface
ICPM	Institut de Physique et Chimie des Materiaux	MPP	massively parallel processors
		MRI	magnetic resonance imaging
IND	Investigational New Drug	MSCD	multiple scattering in cluster diffraction
INEEL	Idaho National Engineering and Environmental Laboratory	MSD	Materials Sciences Division
		MTBE	methyl tertiary butyl ether
IP	interaction point *or* Internet protocol	NCAR	National Conference on the Advancement of Research
IPCC	Intergovernmental Panel on Climate Change		
		NCEM	National Center for Electron Microscopy
IR	infrared	NERSC	National Energy Research Scientific Computing Center
ISO	independent system operator		
ISOL	isotope separator on line	NGF	nerve growth factor
KEK ATF	High Energy Accelerator Research Organization of Japan Accelerator Test Facility	NIEHS	National Institute of Environmental Health Sciences
		NIH	National Institutes of Health
LBNL	Ernest Orlando Lawrence Berkeley National Laboratory	NMR	nuclear magnetic resonance
		NOW	network of workstations
LDA	local density functional	NSAC	Nuclear Science Advisory Committee
LDL	low-density lipoproteins	PAI	plasminogen activator inhibitor
LEED	low-energy electron diffraction	PCM	proximity correlation matrix
LES	large eddy simulation	PCR	polymerase chain reaction
LHC	Large Hadron Collider	PDE	partial differential equation
l'OASIS	Laser Optics Accelerator Systems Integrated Studies	PDSF	Particle Data Storage Facility
		PDT	photodynamic therapy
LOH	loss of heterozygosity	PEEM	photoemission electron microscopy
LP	lean premixed	PEM	proton exchange membrane
LSI	latent semantic indexing	pftp	parallel FTP
MBE	molecular beam epitaxy	PIA	photoinduced absorption
MCD	magnetic circular dichroism	PIC	particle in cell
MCF	Macromolecular Crystallography Facility	PL	photoluminescence
MEK	methyl ethyl ketone	PLD	pulsed laser ablation
MES	molecular environmental science		

PM	particulate matter	StAF	Standard Analysis Framework
POC	particulate organic carbon	STM	scanning tunneling microscope *or* microscopy
QED	quantum electrodynamics		
QSB	quantum suppression of beamstrahlung	SVX	silicon vertex detector
QW	quantum well	TAN	Test Area North
RCSM	regional climate system model	TBA	two-beam accelerator
rf	radio frequency	TCP	Transmission Control Protocol
RHIC	Relativistic Heavy Ion Collider	TGF	transforming growth factor
RIB	radioactive ion beam	UC	University of California
SAGE	serial analysis of gene expression	USAID	United States Agency for International Development
SC	superconducting		
SC/IVR	semiclassical initial value representation	UV	ultraviolet
SCR	silicon-contained rectifier	UZ	unsaturated zone
SIO	Scripps Institute of Oceanography	V-I	volt-amp
SLAC	Stanford Linear Accelerator Center	VIA	virtual interface architecture
SMOKE	Surface Magneto-Optic Kerr Effect	VUV	vacuum ultraviolet
SMP	symmetric multiprocessor	WFO	work for others (LBNL)
SMS	single-molecule spectroscopy	WHOI	Woods Hole Oceanographic Institution
SN	supernova	XAFS	x-ray absorption fine structure
SOI	silicon on insulator	XANES	x-ray absorption near-edge structure spectroscopy
SPAI	sparse approximate inverse		
spFRET	single-pair FRET	XAS	x-ray absorption spectroscopy
SQUID	Superconducting Quantum Interference Device	XES	x-ray emission spectroscopy
		XFH	x-ray fluorescence holography
SR	synchrotron radiation	XMCD	x-ray magnetic circular dichroism
SRRTNet	Synchrotron Radiation Research Theory Network	XPS	x-ray photoelectron energy spectrum
SSC	Superconducting Super Collider	XRD	x-ray diffraction
SSI	Strategic Simulation Initiative	XRFM	x-ray fluorescence microprobe