

DIVISION OF PHYSICAL CHEMISTRY

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Monday Program

Abstracts

PHYS 55 [644953]: Computation driven directed evolution of a beta-lactamase

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The targets of beta-lactam antibiotics, penicillin-binding proteins (PBPs), are believed to have evolved into beta-lactamases, the bacterial resistance enzymes that hydrolyze and therefore inactivate these antibiotics. Both PBPs and beta-lactamases are serine-protease type enzymes that form an acyl-enzyme intermediate. But while beta-lactamases efficiently catalyze hydrolysis of the acyl-enzyme intermediate, PBPs are very poor catalysts of this hydrolysis reaction and so are trapped as the acyl-enzyme intermediate and inactivated. Here we present our results using mixed quantum mechanics/molecular mechanics (QM/MM) calculations to guide the directed evolution of a penicillin-binding protein into a beta-lactamase.

PHYS 56 [642682]: Dissecting molecular recognition with phage-displayed protein libraries

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Libraries of protein variants have been used to identify sidechain residues contributing to receptor function through favorable contacts. Shotgun scanning with phage-displayed libraries of wild-type and alanine residues substituted in specific positions can quantify sidechain contributions to protein function. This 'reverse protein engineering' approach has been used to identify forces responsible for the unusually strong streptavidin-biotin interaction, the stability of M13 bacteriophage coat proteins, and the model protein-DNA interaction engrailed homeodomain binding to a specific DNA sequence. Shotgun scanning with homologous substitutions offers a method to elucidate more subtle forces required for protein specificity and optimal binding. In addition to the structure/activity information obtained from homolog shotgun scanning, the method can be used to rapidly affinity mature polypeptides.

PHYS 57 [642354]: Novel diversity for the creation of protein function

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The directed evolution toolbox contains a number of well-established methodologies (e.g. random mutagenesis and DNA shuffling) for improving such protein properties as stability, catalytic activity and substrate specificity. What are lacking are methods for the creation of new function where no function exists. Traditional directed evolution methods generate diversity by mutating genes and recombining homologous genes but maintaining gene length and order of gene sequences. We are developing two strategies for the introduction of allosteric properties into proteins that utilize diversity created in novel ways: random domain insertion (which utilizes diversity in the order of sequences) and conditional heterodimerization (which utilizes diversity in the gene length).

PHYS 58 [644849]: Computational and experimental analysis of DNA shuffling

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We describe a computational model of DNA shuffling, SHUFFIT, based on the thermodynamics and kinetics of this process. The model independently tracks a representative ensemble of DNA molecules and records their states at every stage of a shuffling reaction. These data can subsequently be analyzed to yield information on any relevant metric, including reassembly efficiency, crossover number, type, and distribution, and DNA sequence length distributions. The predictive ability of the model was validated by comparison to three independent sets of experimental data, and analysis of the simulation results led to several unique insights into the DNA shuffling process. We examine a tradeoff between crossover frequency and reassembly efficiency and illustrate the effects of experimental parameters on this relationship. Furthermore, we discuss conditions that promote the formation of useless "junk" DNA sequences or multimeric sequences containing multiple copies of the reassembled product. We are making SHUFFIT accessible to researchers (<http://www.cchem.berkeley.edu/~schaffer/shuffling>) in order to aid in the design of optimal shuffling reaction conditions.

PHYS 59 [641498]: Nonlinear optical molecular imaging

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We are exploring the use of nonlinear optical spectroscopy for near-field and far-field imaging of soft matter, seeking to exploit the environmental (surface vs. bulk) and molecular (via resonance enhancement) specificity inherent in this approach, combining nonlinear optical spectroscopy with Near-Field Scanning Optical Microscopy to achieve ca. 100 nm spatial resolution, Second Harmonic Generation (SHG) has been used to image membrane-associated perforin granules in Natural Killer Cells, Third Harmonic Generation (THG) has been used to image the distribution of oxyhemoglobin in red blood cells, and Coherent Anti-Stokes Raman spectroscopy (CARS) has been used to selectively image lipid-rich mitochondria in human liver cells. THG has also been employed in studies of the luminescing polymer MeH-PPV to reveal nanoscopic domains of chains exhibiting enhanced delocalization due to ground state overlap. Similar studies are underway in light harvesting dendrimers. Progress in applying these techniques to biological samples will be described.

PHYS 60 [654844]: Nonlinear laser microscopies and spectroscopies of the molecular dynamics of life

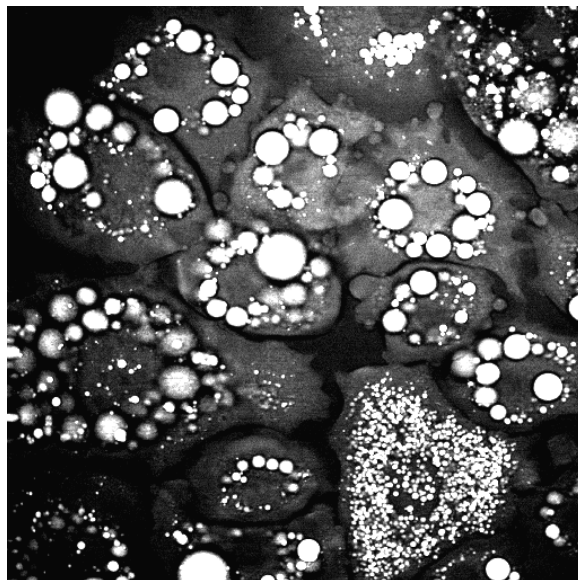
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The dynamics of biomolecular processes can be accessed in vivo by multiphoton laser scanning microscopy and new ultradeep GRIN lens techniques for endoscopy. These methods can access manifestations of disease status deep in tissue, utilizing intrinsic tissue fluorescence and second harmonic generation. Recent applications include mapping and analysis of structural elastin, collagen and microtubules in brain, skin and nascent tumors. Measurements of metabolic state by multiphoton excitation of the autofluorescence molecule NADH in brain has been developed as a tool to study anoxia due to stroke and metabolic strain of neuronal signaling. Fluorescence Correlation Spectroscopy measures the dynamics of molecular mobility and reactions at nanomolar concentrations in solution and in living cells. New methods for observing chemical kinetics of individual enzymes at the high (micromolar) biological substrate concentrations, fast chemical kinetics and efficient single molecule identification techniques based on optical nanostructures are to be reported.

PHYS 61 [644146]: Coherent anti-Stokes Raman scattering (CARS) microscopy: Cellular imaging with vibrational contrast

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CARS microscopy is becoming a valuable tool for visualizing live cells with chemical selectivity. A vibrational sensitive technique, CARS microscopy generates images of unstained biological samples with high sensitivity and high 3D spatial resolution. In this contribution we discuss the most recent advances in CARS microscopy and its applications to cell biology.



PHYS 62 [639768]: Simultaneous force and fluorescence dynamics of single antigen-antibody pairs

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Interactions between molecules depend on many variables including separation distance, orientation, conformation, and local environment. Two single molecule techniques, atomic force microscopy (AFM) and single-molecule fluorescence spectroscopy (SMFS) are sensitive to those parameters. The combination of AFM force spectroscopy and SMFS provides a more complete description of the interaction between molecules and the effects of molecular orientation, conformation, and dynamics on the interaction forces as a function of separation distance. Here we present a combined AFM and scanning confocal microscope capable of simultaneous single molecule detection and manipulation. Using a simple system, antibodies directed against a fluorophore, we investigate the coupled intermolecular interactions and fluorescence quenching dynamics of a ligand-receptor pair during forced binding/unbinding. We present simultaneous SMFS measurements on the AFM forced-unbinding of single antigen-antibody pairs in aqueous buffer and examine correlations between fluorescence intensity, separation distance, applied load, and binding state.

PHYS 63 [635843]: Femtosecond pulse shaping approaches to multiphoton imaging

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Multiphoton imaging with fluorescence detection has proven to be a powerful method for moderately deep tissue imaging (several hundred microns) with molecular specificity. However, many important endogenous biomolecules (such as NAD) do not fluoresce. We have shown that a variety of femtosecond pulse shaping methods permit high sensitivity detection of two-photon absorption, instead of fluorescence, which opens up a wider range of molecular targets. It also facilitates use of lower excitation wavelengths, which permit greater tissue penetration.

PHYS 64 [642137]: Approaches to infrared and visible reflectance spectroscopic imaging

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For probing, non-invasively, molecular heterogeneity in the micron to millimeter range, we have developed in our laboratory several spectroscopic techniques involving both infrared and visible reflectance spectroscopies. The vibrational infrared approaches couple appropriate microscopes and dedicated spectroscopic instrumentation specifically for examining biological tissue, for monitoring dynamic processes and for characterizing polymeric mixtures, while our novel visible reflectance spectral imaging technique is used in the context of clinical, real-time in vivo applications. Imaging methods are relative newcomers to the vast array of particularly vibrational techniques. While they inherit the versatility and data bases of traditional single point detection approaches, the integration of digital imaging technologies allows new perspectives in spectral interpretations. We shall first discuss Fourier transform (FTIR) spectroscopic imaging utilizing mid-infrared step-scan and continuous-scan interferometry coupled to infrared microscopes and appropriate infrared focal-plane array (FPA) and linear array detectors. This integrated instrumentation represents basically a multiplex/multichannel approach for acquiring experimental data. Secondly, we shall describe a visible reflectance spectroscopic methodology based upon liquid crystal tunable filter (LCTF) technology and two-dimensional CCD detection.

PHYS 65 [643353]: Supermolecular stereochemistry in liquid crystals

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Tilted smectic liquid crystals (LCs) possess polar symmetry, and a macroscopic electric dipole moment, when the molecules are enantiomerically enriched. Recently, a class of chiral smectic LCs composed of "bent-core" achiral or racemic molecules has been discovered. In the field these LCs are termed "banana phases," and studies suggest that a large variety of interesting new phases are formed. Most of the known banana phases are antiferroelectric, which according to our models is due not to Coulombic forces but rather entropic considerations. The directed design, synthesis, and structure of a ferroelectric banana phase will be described. In this phase the presence of a spontaneous splay in the polarization causes periodic layer-spacing fluctuations and undulating smectic layers with a wavelength of 500Å.

PHYS 66 [636954]: Liquid-crystalline phases of anisotropic inorganic Nanocrystals

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In recent years there have been several advances that permit the preparation of anisotropic rod or disk shaped nanocrystals with tight control of the size distribution and the aspect ratio. These nanocrystals will spontaneously form lyotropic liquid crystalline phases at sufficiently high density in solution. These liquid crystalline phases are of considerable interest from both fundamental and practical points of view. Compared to conventional organic or macromolecular liquid crystals, the electric, optical, and magnetic properties can cover a much wider range. The nature of the forces between the nanocrystals can vary considerably depending upon the polarizability, dipole moment, and magnetization of the nanocrystals. This talk will describe recent work to determine the phase diagrams for CdSe nanorods, as well as for iron oxide and Co nanodisks. In addition, work to produce macroscopic alignment with external electric and magnetic fields of the inorganic nanocrystal liquid crystal phases will be described

PHYS 67 [644127]: Tubelets: A new phospholipid tubule intermediate

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A novel sample preparation technique enables attainment of unprecedented detail in scanning-electron microscopy probes of the ribbon-like multilayer phospholipid membranes that wind helically to form the closed cylinders known as "tubules."

These lyotropic liquid-crystalline structures are shown to exist principally in two configurations: 1) helically-wound, cylindrical segments that we interpret as tubule precursors; and 2) axially-wound "gaussian" segments. A single ribbon typically alternates between these states, and the chiral sense of these windings can change abruptly at the segment junctions.

PHYS 68 [642195]: Phase transitions and molecular detection in a lipid membrane-derivatized colloid
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Two – dimensional dispersions of lipid membrane – derivatized silica beads exhibit colloidal phase transitions that are governed by membrane surface interactions. The collective phase behavior serves as a cooperative amplifier that produces a readily detectable response from a small number of molecular events on the membrane surface. Using direct optical imaging, we observe multiple near-equilibrium phases and find that protein binding to membrane – associated ligand at densities as low as 10^{-4} monolayer can trigger a phase transition. Statistical analysis of bead pair distribution functions enables quantitative comparison among different membrane systems and reveals subtle, pre-transition effects.

PHYS 69 [632402]: Geometric approach to self-assembly
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We propose a heuristic explanation for the numerous non-close-packed crystal structures observed in various colloidal systems. By developing an analogy between soap froths and the soft coronas of fuzzy colloids, we provide a geometrical interpretation of the free energy of soft spheres. Within this picture, we show that the close-packing rule associated with hard-core interaction and positional entropy of particles is frustrated by a minimum-area principle associated with the soft tail and internal entropy of the soft coronas. We find that the A15 lattice, known to be area minimizing, is favored for a reasonable range of model parameters and so it is among the possible equilibrium states for a variety of colloidal systems. We extend these ideas to diblock copolymers and find new, stable sphere-like phases.

PHYS 70 [644529]: Nematic-isotropic transition in liquid crystalline elastomers
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Anisotropic freestanding films and fibers of nematic elastomers from laterally attached side-chain polymers show reversible shape change. The orientational order of the liquid crystal side groups imposes a conformational anisotropy in the polymer backbone. When a large change in the order parameter occurs, as at the nematic-isotropic phase transition, there is a concomitant loss of order in the backbone which results in a contraction of the film/fiber in the direction of the director orientation. The induced strain varies smoothly across the NI transition due to the quenched disorder combined with the effects of applied and internal stresses. Monte Carlo simulations show that this smoothening of the transition is consistent with random-bond disorder. Strains can also be induced in a nematic elastomer film via the reorientation of the mesogens by an applied voltage. The effect of the random-field disorder in this case near the N-I transition will be discussed.

PHYS 71 [634890]: Influence of oxygen vacancies on surface and interface reactions on the rutile TiO₂(110) surface

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Defects such as oxygen vacancies often dominate the electronic and chemical properties of transition-metal oxide surfaces. I will review recent studies on a prototypical model oxide surface - rutile $\text{TiO}_2(110)$ - where we have exploited our high-resolution STM to study how oxygen vacancies influence surface and interface reactions. A novel and surprising O_2 -mediated diffusion mechanism of oxygen vacancies on $\text{TiO}_2(110)$ will be presented. Bridging oxygen vacancies are found to be the active nucleation sites for Au clusters on the rutile $\text{TiO}_2(110)$ surface and we find that each vacancy site can bind 3 Au atoms on average. The change in morphology of the gold nano-clusters, exposed to CO and O_2 , both under UHV and high pressure conditions, will be discussed.

PHYS 72 [639814]: Structure and reactivity of metal clusters at oxide surfaces characterized by time-resolved DXAFS and STM

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In this study we attempted to obtain the information on how and when cluster structures change during chemical processes, which will help to discover unidentified chemistry of dynamics of catalytically active metal clusters at surfaces. We have succeeded in monitoring time-dependent Ru and Rh cluster structures at oxide surfaces in a molecular scale by time-resolved energy-dispersive X-ray absorption fine structure (DXAFS). This paper also reports the structure and reactivity of Pt nano-clusters prepared by metal-organic chemical vapor deposition (MOCVD) and metal vapor deposition (MVD) on $\text{TiO}_2(110)$ surfaces, which were characterized by scanning tunneling microscopy (STM).

PHYS 73 [635032]: Structures and complexes of size-selected silver clusters

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Size-selected metal cluster were prepared by mass-filtering cations from a sputtered cluster beam, retarding the clusters so as to minimize fragmentation upon impact, then neutralizing the positively charged clusters in a stream of thermionic electrons in the presence of cold rare gas such as argon. Using this technique we were able to determine unequivocal structures for Ag_5 and Ag_7 , show that the dimetalcarbonyl formed from size-selected Fe dimers is the octacarbonyl rather than the enecarbonyl and determine upper bounds for the SERS enhancement resulting from resonance enhancement alone (<1000).

PHYS 74 [659061]: The structure of Au in Au/titania catalysts, used in the epoxidation of propene in H_2/O_2 mixtures

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Traditionally, gold has been regarded as a beautiful metal without any potential in catalysis. Recently, this picture has changed completely. It was discovered that nanosize clusters of gold are exceptionally active. For instance, in the presence of the rightly prepared Au catalysts CO oxidation occurs at high rates below 0 °C. Au/titania catalysts show potential in a commercially extremely important reaction, viz., the production of ethene epoxide from propene and a mixture of hydrogen and oxygen.

Results will be presented from a thorough characterization of the gold clusters by a combination of XPS, TEM and ¹⁹⁷Au Mössbauer absorption spectrometry. The deposition-precipitation method used lead to gold particle sizes ranging from 3 to 6 nm. The mechanism is based on bifunctional catalysis: Au catalyses the formation of

hydroperoxide-like species from oxygen and hydrogen, while the epoxidation of propene takes place at the titania support. It will be shown that all information indicates that metallic gold is the active phase during epoxidation.

PHYS 75 [644377]: Shape, sintering and SERS from size-selected metal clusters on oxide supports

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I will discuss our recent progress in probing the shape and sintering of size-selected Ag and Au clusters supported on titania surfaces using STM. We probe the evolution of the cluster shape as a function of temperature, surface conditions and defect density. We have also probed the cluster shape under catalytic conditions in the oxidation of unsaturated hydrocarbons such as ethylene and propylene. In addition we have used a metal tip over individual clusters to enhance the electric field within the tip-cluster gap by several orders of magnitude. We have used this enhanced field to record the SERS spectrum of molecules within the gap.

PHYS 76 [642024]: Phase transition of reaction dynamics in glassy environment

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We derive the exact evolution equation and the boundary condition for a reactive continuous time random walker with arbitrary waiting time distributions for transport and reaction processes. Expressions for the probability distribution function and the survival probability of the reactive continuous time random walker are also presented. The results predict a novel phase transition in the behavior of the relaxation dynamics and ultimate survival probability.

PHYS 77 [644903]: Effects of dynamical heterogeneity on translational diffusion and single-molecule studies in glass forming liquids

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Based upon the coarse-grained model, we study translational and rotational diffusions of probe molecules in glass forming liquid systems. In particular, within purely dynamical and geometrical aspects, we present novel explanations of the breakdown of the Stokes-Einstein relation that has been observed in many glass forming liquid systems near the glass transition temperature. We have also studied implications of the dynamical heterogeneities on recent single molecule experiments of glass forming liquids. We investigate the distribution of the dynamical heterogeneities probed by single probe molecules over different coarse-graining timescales through numerical simulations. Based on our simulation results, we propose a new experimental measurement involving correlations among single probe molecules that will provide informations on the distributions of dynamical heterogeneity.

PHYS 78 [638941]: Self-diffusion near T_g in single component glass formers

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The self-diffusion coefficient is arguably the single most important measure of mobility in a liquid. We present the first direct measurement of self-diffusion of a single-component glass-forming liquid at the glass transition temperature. Forward Recoil Spectrometry (FRoS) is used to measure the concentration profiles of deuterio and protio 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene (TNB) following annealing-induced diffusion in a vapor deposited bilayer. These experiments extend the range of measured diffusion coefficients in TNB by 6 orders of magnitude. While rotational correlation times have previously been found to track the viscosity, these new results indicate a decoupling of translational diffusion from viscosity or rotation. At T_g, D is 500 times larger than expected

from the Stokes-Einstein equation. These results are qualitatively consistent with previous measurements of dye diffusion in TNB and explain the unusual temperature dependence of crystal growth rates in TNB.

PHYS 79 [642295]: Single-particle dynamics in deeply supercooled liquids

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Photoluminescence from metallic nanoparticles with nanometer diameters has been used to study orientational dynamics in a deeply supercooled liquid, 4,4'-(octahydro-4,7-methano-5H-inden-5-yliden) bisphenol dimethyl ether (ODE). We explore the dependence of the bulk orientational correlation time on the bulk ODE viscosity to show that nanoparticles can provide a useful probe of local dynamics, and we discuss single-particle orientational diffusion trajectories. We will also compare the information available from two- and three-dimensional orientational trajectories.

PHYS 80 [660384]: Quenching-in of different high T complexities of glassformers for leisurely study at lower temperatures

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We describe a series of experiments on glass-forming liquids that are motivated by a common idea. The idea is that of trapping in a high enthalpy, high entropy, state of the system by quenching to the glassy state at extreme rates, and then observing the way the system evolves at low temperatures during a controlled annealing procedure. In this manner, events that normally occur during change of temperature may be observed occurring during passage of time, at much lower temperatures. At these low temperatures, the smearing effects of vibrationally excited modes may be greatly reduced. For simple glassformers we study both relaxational properties and vibrational properties and find that the high fictive temperature states are characterized by short relaxation times (already known) and considerably more intense boson peaks (less well known) [1]. The thermodynamic consequences of the increased populations of these low frequency modes are examined with the help of computer simulation and normal mode calculations on model glassformers. Behavior in the vibrational DOS at constant pressure is strikingly different from that at constant volume. For glassformers that can exhibit liquid-liquid transitions, one can use the cold equilibration approach to determine the fragility of the high temperature phase, and the enthalpy of the liquid-liquid transition, see ref.2. Finally, for solutions of complex molecules with interesting internal molecular transitions, such as proteins, we can quench in the unfolded states and then, using special non-crystallizing solvents, observe the molecular reorganization to low energy states as it occurs at temperatures far below the normal folding temperature [3].
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PHYS 81 [644985]: Anatomy of a string: Correlated particle motion in simulated supercooled liquids

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We present new results of a detailed investigation of correlated particle motion in model supercooled liquids studied via molecular dynamics simulation. We investigate in particular the tendency for correlated motion to occur in strings. We present a detailed analysis that elucidates how and why strings form, the degree of coherence of particle motion within strings, the lifetime of strings, and the role of strings in facilitating structural relaxation in the liquid. [1] Y. Gebremichael, M.I. Vogel and S.C. Glotzer, "String-like correlated particle motion in a Dzugutov liquid," preprint.

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PHYS 82 [658814]: Evolutionary perspectives on protein folding, structure, and thermodynamics

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Proteins fold into their native-state conformations in milliseconds to seconds, ignoring theoretical estimates that this process should take many times the age of the universe. Much work is directed to understanding how proteins are so much smarter than theorists, who cannot even reliably predict what the final folded states will be. Proteins have one major advantage over theorists - proteins have been working on this problem for billions of years. We can consider different ways in which proteins may have evolved to solve the protein-folding problem. Using simple theoretical models, we can show how neutral evolution and population dynamics combined with the need to fold can explain many of the observed properties of proteins, including the way proteins fold, the distribution of observed protein structures, the marginal stability of proteins, and how the evolutionary robustness of protein structures co-exists with sequence plasticity.

PHYS 83 [644418]: Protein building blocks for recombination

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In vitro recombination is a powerful tool for tuning and optimizing protein functions. It promotes the rapid accumulation of beneficial traits from multiple parents onto a new single offspring. Recombination also plays a key role in natural evolution in the generation of diverse antibodies, synthases, and proteases through the swapping of well-defined structural domains. However, while there have been several approaches to identifying the building blocks of proteins, the principles that govern whether a polypeptide fragment can be exchanged among different proteins remain unclear. We have recently developed a computational algorithm called SCHEMA for identifying the structural units that can be swapped among homologous proteins without disrupting the three-dimensional structure of the protein. This talk will discuss the SCHEMA method and its application in guiding recombination experiments.

PHYS 84 [644428]: Exploring sequence space by structure-guided recombination

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Anecdotal evidence from DNA-shuffling experiments suggests that recombination can rapidly accumulate beneficial mutations onto a single offspring and possibly find novel and beneficial combinations of amino acids that are neutral in their original, parental contexts. Little information exists, however, on the relationship between mutation level and evolution of protein function, i.e. how evolution of function scales with the number of effective mutations incorporated by recombination. We are using structure-based tools to identify polypeptide elements that can be swapped among related proteins without disrupting their three-dimensional structure. By recombining these elements in a combinatorial fashion we are creating well-defined libraries of diverse sequences (using distantly-related β -lactamase or cytochrome P450 homologs as parents), a large fraction of which are predicted to retain parental fold. We are analyzing the structures and activities of proteins in these chimeric libraries, and investigating whether these proteins can display interesting behaviors, including ones not known in nature.

PHYS 85 [644365]: Focused saturation mutagenesis for antibody affinity maturation

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There is substantial and expanding activity in the development of antibody drugs, and therapeutic efficacy is often directly related to antigen binding affinity. We have demonstrated previously that directed evolution by yeast surface display is a powerful method for identifying mutant antibodies with extremely high affinity, however such mutants often possess functionally consequential mutations in framework residues that raise the specter of human immunogenicity along the clinical development pathway. It is of interest to identify which sites in the complementarity determining regions (CDRs) can be mutated to obtain improved affinity. We have taken both computational and experimental approaches to finding those sites most amenable to mutagenic improvement, using as model systems the 4-4-20 antibody against fluorescein and the D1.3 antibody against lysozyme.

PHYS 86 [642659]: Evolution and mis-evolution of antibodies in the immune system

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We introduce a model of protein evolution to explain limitations in the immune system response to vaccination and disease. The phenomenon of original antigenic sin, wherein vaccination creates memory sequences that can *increase* susceptibility to future exposures to the same disease, is explained as stemming from localization of the immune system response in antibody sequence space. This localization is a result of the roughness in sequence space of the evolved antibody affinity constant for antigen and is observed for diseases with high year-to-year mutation rates, such as influenza.

PHYS 87 [636616]: Doing chemistry with MCSCF wavefunctions

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The primary driving force behind several decades of work on MCSCF methods has been this wavefunction's utility in describing chemical reactions including bond breaking. However, bond breaking is just one example of electron unpairing/re-pairing, and indeed MCSCF wavefunctions are also useful for the description of excited states or ionization processes. A number of technical improvements to programs for the generation of MCSCF wavefunctions will be presented, including scalable integral transformations, improved CI methodology permitting increasingly larger active spaces, strategies for orbital optimization, and treatments for dynamic correlation. Some speculation about future progress will be given. Although MCSCF's success in treating reactive channels is well known, this method also provides useful chemical interpretations. Indeed, it is one of the strong points of MCSCF that it involves an active space, allowing one to focus attention on the reacting electrons and the shapes of the orbitals that hold them. Orbital invariance within the active space (and within the doubly occupied space) permits localized or natural orbital generation. Expressing the wavefunction in terms of the former, in particular, leads to a great deal of chemical insight into bonding patterns. This will be demonstrated by examples drawn from previous and current research using MCSCF methods.

PHYS 88 [643518]: Assessing quantum chemical methods for bond breaking: Single-reference, multi-reference, and minimalist models

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Various single- and multi-reference methods have been evaluated for their performance in bond breaking reactions by comparing to full configuration interaction potential energy curves, which represent the exact solution of the electronic Schroedinger equation for a given one-particle basis set. Even in the simplest case of breaking a bond to a hydrogen atom, the best unrestricted single-reference method in common use, UCCSD(T), exhibits nonparallelity errors of about 3 kcal/mol. Available multi-reference methods provide significant improvement, although at the price of increased complexity and computational cost. New, minimalist models of bond breaking in a generalized restricted active space configuration interaction (RAS CI) framework will be described, and various choices of orbitals for both single- and multi-reference approaches have been explored. Finally, different basis sets have been compared for their performance in full configuration interaction benchmarking, and natural orbitals are found to dramatically improve predictions of molecular properties.

PHYS 89 [642106]: Direct CI and MCSCF method for multiple active spaces with variable occupations

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In order to reduce the number of ineffective configurations in a priori generated configuration spaces, a direct configuration interaction (CI) method has been developed which limits the electron occupations of orbital groups making up a total active space. A wavefunction is specified by firstly partitioning an active space into an unrestricted number of orbital groups and secondly by providing limiting values, in the form of minima and maxima, for the electron occupancies of each group. The CI problem corresponding to all possible determinants satisfying these conditions is solved in a fully direct manner by the use of Slater-Condon expressions in conjunction with single and double replacements. This CI approach, termed Occupation Restricted Multiple Active Space-CI (ORMAS-CI), has also been linked with orbital optimization programs to produce the ORMAS-SCF method. Several applications will be presented demonstrating that large CI spaces may be drastically reduced with negligible loss of accuracy.

PHYS 90 [636419]: String product space self-consistent field method and second-order perturbation theory

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A multiconfiguration self-consistent field (SCF) method is presented where the string product space (SPS), the product space of alpha- and beta-string spaces, is used as a variational space. The computational effort for wavefunctions is significantly reduced compared with the complete active space self-consistent field (CAS-SCF) method, and yet the accuracy is comparable to the CAS-SCF case. A computational scheme and some numerical examples for potential energy surfaces and excitation energies are shown. Furthermore, a multiconfigurational quasi-degenerate perturbation theory (MC-QDPT) [Nakano, J. Chem. Phys., 99, 7983 (1993)] using the SPS-SCF reference wavefunctions is also presented. The inclusion of dynamic correlation by the second-order MC-QDPT scheme fairly improves the SPS-SCF results, giving chemical accuracy.

PHYS 91 [643594]: Large full valence spaces without configurational deadwood

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Molecular electronic structures are described by wavefunctions consisting of (i) zeroth-order terms (SCF or MCSCF) and (ii) refinement terms (accounting for dynamic correlation). In most systems, the fundamental understanding of bond forming and breaking as well as reaction paths emerges from the zeroth-order terms. A classical and effective zeroth-order choice is the optimized full valence-space of deformed minimal-basis atomic orbitals. While even this limited configuration space grows too large for practical use in moderately sized molecules, its growth is largely due to vast increasing amounts of ineffective configurations. We have developed a systematic procedure for eliminating a-priori all configurational deadwood and thereby reducing the configurational expansion by orders of magnitude. The reduction fraction moreover increases with the size of the molecule, making larger systems accessible. In this context, we have shown CI expansions generated from split-localized orbitals to converge faster than those generated from natural orbitals.

PHYS 92 [644266]: Imaging, spectroscopy and dynamics of single biomolecules: From in vitro to in vivo studies

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Our single-molecule experiments have shown that an enzyme is a dynamical entity whose conformation and enzymatic rate undergo constant fluctuation over a broad range of time scales. The phenomenon has been observed in several systems: cholesterol oxidase, flavin reductase, and exo-nuclease. Various single-molecule experiments, such as observing enzymatic turnovers by fluorescence, probing conformational dynamics by photoinduced electron transfer, and studying DNA/enzyme interaction by a simple flow assay, have led to new insights into the fluctuating enzymes. We are conducting single-molecule experiments in live cells. Our results on imaging the expression of a single gene in a bacterium cell will be presented.

PHYS 93 [635853]: What can we learn about protein folding from single-molecule FRET trajectories?

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We develop single-molecule fluorescence spectroscopy as a tool for studying protein folding dynamics. Protein molecules are specifically labeled with donor and acceptor probes for fluorescence resonance energy transfer (FRET). The labeled molecules are trapped within surface-tethered lipid vesicles. This immobilization method allows extended observation periods, while minimally affecting the properties of the trapped molecules. Protein molecules are prepared at the denaturation mid-point using a chemical denaturant, and their FRET trajectories show transitions between a broad range of intermediate states, which can be classified in two groups, the ‘folded’ ensemble and the ‘unfolded’ ensemble. This complex behavior provides direct evidence for the availability of multiple folding pathways, as predicted by theory. Further, statistical analysis of trajectories and transitions enables us to characterize the diffusional dynamics of proteins on their energy landscape.

PHYS 94 [643209]: Emerging frontiers in single-molecule fluorescence imaging

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In the past dozen years, single-molecule fluorescence techniques have been used to explore heterogeneity, kinetics, local orientations, energy transfer, and the behavior of single quantum systems in fields ranging from biophysics, to quantum optics, and to materials science. Recently, some groups have begun to explore the behavior of individual fluorescent molecules in the challenging environment of living cells. By extrinsic labeling of an antigenic peptide, we have completed a detailed study of the diffusion of single copies of major histocompatibility complexes of type II (MHCII) in the membranes of CHO cells. The results from this study bear on fundamental properties of the cell membrane, in particular on the presence of significant confinement restricting the motion of the MHCII transmembrane proteins and the role of cholesterol. In recent work, we have discovered a new class of fluorophores amenable to single-molecule imaging in polymeric hosts, with potential for use in biological environments.

PHYS 95 [643293]: Single molecule protein folding

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Protein folding is an inherently heterogeneous process because of the very large number of microscopic pathways that connect the myriad of unfolded conformations to the unique conformation of the native structure. In a first step toward the long-range goal of describing this pathway distribution experimentally, we have measured Förster resonance energy transfer on single, freely diffusing or flowing molecules. From the results we are able to obtain properties of the free energy surface for folding that have not or cannot be obtained from ensemble experiments.

PHYS 96 [643573]: Single molecule fluorescence polarization for real-time structural dynamics of macromolecules

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Novel total internal reflection fluorescence microscopes can detect dynamic signals from single fluorophores. This technology has now achieved 1 - 2 nm positional precision at 0.5 s time resolution and 5° – 10° angular precision at 20 ms time resolution. Combined with methods to insert fluorescent probes into macromolecules at known local orientation without destroying their function, these advances allow mechanistically relevant structural dynamics to be detected in functioning complexes. Myosin V is a molecular motor that processively carries vesicular cargoes within brain and pigment cells. During motility, a calmodulin (CaM) light chain on myosin V switches abruptly between two discrete three-dimensional orientations. Translocation of the CaM alternates between larger and smaller steps. These results provide strong evidence that processive motility is due to hand-over-hand stepping generated by a tilting CaM lever arm. The techniques should be applicable to many other supra-molecular machines. Work of many coworkers and collaborators and support by the NIH, NSF, MRC are gratefully acknowledged.

PHYS 97 [654974]: Clusters: Insights into surface reactions and catalyst involving oxygen transfer processes

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Small clusters are comprised mainly of surface atoms or molecules and their study can provide useful information related to surface science. As a complementary approach to conventional surface studies widely used in the field of catalysis, it is becoming increasingly recognized that cluster science can also help elucidate the physical and chemical properties of condensed phase catalysts and, can provide detailed information on the mechanisms of reactions and the nature of various reaction sites that enables certain catalytic materials to be especially effective. In addition, the possible direct use of clusters as catalysts has aroused interest due to the difference in reactivities often observed for nanoscale materials compared to conventional bulk catalysts.

PHYS 98 [641163]: Infrared spectroscopy of size-selected cluster-adsorbate complexes

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Weakly bound complexes of the form $Mx^{+}-(L)y$ ($M=Fe, Ni, \text{ etc.}; L=CO_2, C_2H_2, H_2O, \text{ benzene, etc.}$) are prepared by laser vaporization in a pulsed-nozzle cluster source. These species are mass analyzed and size-selected in a reflectron time-of-flight mass spectrometer. Clusters are photodissociated at infrared wavelengths with a Nd:YAG pumped infrared optical parametric oscillator/amplifier (OPO/OPA) laser or with a tunable infrared free-electron laser. In the past, it has been impossible to study the infrared spectroscopy of molecules like these because the density produced in the gas phase is too low to detect. Now, however, the intense infrared available from OPO's or free-electron lasers makes it possible to do either single-photon or multiphoton photodissociation spectroscopy. For example, $Fe^{+}-(CO_2)_x$ complexes absorb near the free CO_2 asymmetric stretch near 2349 cm^{-1} but with an interesting size dependent variation in the resonances. Small clusters have blue-shifted resonances, while larger complexes have additional bands due to surface CO_2 molecules not attached to the metal. Intracuster reactions are observed for complexes of nickel or cobalt that couple acetylene molecules to make pi-bonded cyclobutadiene. $M^{+}(\text{benzene})$ and $M^{+}(\text{benzene})_2$ ions ($M=V, Ti, Fe$) represent half-sandwich and sandwich species, whose spectra are measured near the free benzene modes. These new IR spectra and their assignments will be discussed as well as other new IR spectra for similar complexes.

PHYS 99 [667344]: Size-selected cluster models for nm-scale catalysts: Adsorption & reactions in an atmospheric-pressure flow reactor

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Gas-phase clusters can offer benchmark-level understanding of many important gas-solid processes, including those implicated in operating catalysts. Reactions of selected clusters are measured mass-spectrometrically over a range of size-, composition-, coverage- and charge-states. Molecular adsorbates are introduced in an atmospheric-pressure flow-reactor, such that thermal adsorption kinetics and equilibria are measured over the entire range of relevant temperature and coverage. Adsorption isotherms and kinetic parameters are related to catalytic activity and compared with predictions of high-level theory. In this paper, selected results will be presented on the following systems: gold-cluster air-purification catalysis; carbon clusters as model soot-catalysts for SO₂ oxidation; vanadium-oxide cluster redox reactions; and sodium-chloride cluster reactions relevant to atmospheric aerosol catalysis.

PHYS 100 [657790]: Infrared spectroscopy on size-selected gas-phase clusters and cluster adducts

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There are a variety of methods to spectroscopically investigate molecules and clusters in the gas-phase. In the infrared (IR) spectral region, methods are often limited by the availability of bright and tunable light sources. We use pulsed radiation from the free-electron laser FELIX to measure vibrational spectra of size-selected gas-phase clusters. FELIX has a tuning range from 2000 to 40 wavenumbers. The light comes in 5-microsecond-long macropulses energies of up to 150 mJ. This makes FELIX the ideal tool to resonantly pump large amounts energy into gas-phase species. This absorbed energy can then cause secondary processes such as fragmentation or ionization to occur. Measuring their yield as a function of excitation wavelength gives an IR spectrum of the molecule or cluster. Here, we report on IR spectra of transition metal-oxide clusters, as well as spectra of the clusters complexed with small organic molecules.

PHYS 101 [643894]: Atomic-scale structure of RuS₂ nanoclusters from Ru₃(CO)₁₂ and S₂ precursors

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RuS₂ has been shown to be the most active catalyst for hydrodesulfurization. Using XPS and STM, we studied the formation and the structure of RuS₂ nanoclusters supported on an Au(111) template, which are of interest as a model catalyst. The adsorption and decomposition of Ru₃(CO)₁₂ on Au(111) surface yields islands of non-coalescing 3D metallic Ru nanoclusters with narrow size distribution. After exposure to S₂ at room temperature, Ru/Au(111) reacts with sulfur, forming RuS₂ characterized by 1.6 eV shift in binding energy of Ru 3d core levels. In contrast, the Ru(0001) surface does not form sulfide under the identical conditions. The STM studies show that the morphology of metallic ruthenium cluster-islands is preserved after reaction with sulfur. Upon annealing, small part of sulfide is found as truncated triangular islands. Atomic-resolution STM images show that these clusters are one layer thick RuS₂ nanocrystallites with their (111) plane parallel to the Au(111) substrate.

PHYS 102 [643258]: Size-, packing density-, and shape-controlled nanocrystal-coated nanotube fabrication using molecular recognition and conformation control of sequenced peptides

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With recent interest in seeking new biologically inspired, device fabrication methods for nanotechnology, we are developing a new biological approach to fabricate metal nanowires by using sequenced peptide nanotubes as templates. The sequenced peptide molecules were assembled as nanotubes and the biological recognition of the sequenced peptide toward metals lead to efficient metal nanocrystal coatings such as Au, Ag, Cu, Ni on the nanowires. Highly crystalline metal nanocrystals were uniformly coated on the peptide nanotubes with the high-density coverage. The conformations and the charge distributions of the sequenced peptide on surfaces, determined by pH and ion concentrations in the growth solutions, control the size and the packing density of nanocrystals. In the

case of Ag nanocrystals, the shape of nanocrystals was also controlled. It should be noted that metallic nanocrystals in diameter around 6 nm are in the size domain to observe significant conductivity change by changing the packing density, and therefore this system may be developed to a conductivity-tunable building block. We believe this simple metal nanowire fabrication method can be applied to various metals and semiconductors with peptides whose sequences are known to mineralize specific ions.

PHYS 103 [638678]: Fluctuating ages in glassy dynamics

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Firstly, I shall summarize some of the main features of the averaged and global non-equilibrium relaxation of glassy systems, weakly sheared viscous liquids and weakly tapped granular matter, and how these results have been successfully reproduced with a mean-field-like analytic approach. Secondly, I shall explain the outcome of more refined experimental and numerical measurements that point at examining the dynamics at a mesoscopic scale. Finally, I shall discuss a theoretical approach for the local mesoscopic dynamics and how its predictions compare to numerical and experimental results.

PHYS 104 [642603]: Emergence of glassy dynamics in a lattice model with constraints

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The glass transition in supercooled liquids is heralded by non-exponential relaxations and a growth of relaxation times characterized by the Vogel-Fulcher law. We have studied the stochastic dynamics of a lattice model with locally jammed states: i.e., local rearrangements cannot change the state. We find that the constraints on the rearrangements lead to relaxation processes dominated by traps that are entropic in origin. Using results of simulations, a master equation describing the order parameter dynamics has been derived. The longest relaxation time can be calculated exactly from this master equation and exhibits a Vogel-Fulcher divergence. The origin of this divergence can be traced back to "effective" barriers that diverge. The nature of the order parameter relaxation can also be calculated exactly and is non-exponential. I will compare these dynamics to the landscape dynamics observed in supercooled liquids.

PHYS 105 [644067]: Slow-relaxation and non-hydrodynamic behavior

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This talk discusses dynamic approaches to calculate slow relaxation and stochastic models to describe non-hydrodynamic behavior. (1) Systematic approaches are used to calculate power-law and stretched exponential relaxation of many-body systems. In the hydrodynamic regime, Gaussian factorization is applied to evaluate memory kernels and is shown to recover the mode coupling effects. (2) A central result of this analysis is the relationship between the non-Gaussian behavior of the bilinear density correlation function and the non-exponential nature of linear hydrodynamic modes. This relation reveals the nature of non-linear measurements within the validity of the mode-coupling approximation and suggests the need for new dynamic models far away the hydrodynamic limit. (3) On the phenomenological level, the motion of Brownian test particles in a solvent near the glass transition can be modeled by diffusion in a stochastic potential with spatial-temporal correlation. The one-particle diffusion and two-particle correlation exhibit signatures indicative of a glassy system. The connection of the stochastic diffusion model to other hopping models are discussed and their limitations in describing realistic liquids are examined.

PHYS 106 [643990]: L'evy distribution of single molecule line shape cumulants in glasses

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Russian Academy of Sciences, Lothar Kador, Institute of Physics and Bayreuther Institut für Makromolekulare Forschung (BIMF), Institute of Physics and Bayreuth University of Bayreuth, and Robert J. Silbey, Department of Chemistry, Massachusetts Institute of Technology

Experimental advances have made it possible to measure the spectral line shape of a single dye molecule embedded in different types of glassy materials. Because each individual molecule is in a unique static and dynamic environment, the line shapes of chemically identical single molecules varies from molecule to molecule. The problem of ensemble averaging is at last removed. Using the Geva-Skinner model we examine the statistical properties of line shapes of single molecules in a low temperature glass described by the standard tunneling model. In this model, a random distribution two level systems (TLS) interacts with the molecule via long range interaction (e.g., dipolar). We show that Levy statistics fully characterizes the properties of the single molecule spectral line both in the fast and slow modulation limits. Computer simulation show that the slow modulation limit is valid for certain parameter set relevant to experiment. Analyzing recent the experimental data, obtained by the groups of Vainer and Kador, we show that Levy statistics is compatible with the experimental data. The relation between Levy statistics and long range interacting systems is not limited to our model system, we discuss other long range interacting systems where this relation was overlooked. The experiment and data analysis yield: (i) direct evidence for the existence of TLSs in glasses, and (ii) proof that standard tunneling model predictions work well (a few molecules being interesting exceptions).

PHYS 107 [655452]: Nanoscale noise in glass

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A number of recent experiments and simulations strongly support the idea that dynamics are spatially heterogeneous in glassy materials. Relaxation times appear to be correlated over a few nanometers, supportive of the notion of cooperatively-rearranging-regions (CRR) containing of order 100 molecules. But details of the local cooperative dynamics are still mysterious. Certain issues, such as the heterogeneity lifetime, and whether local relaxation within a CRR is exponential, remain controversial. I will describe experiments in which molecular cooperativity was directly observed near the glass transition, through nanoscale probing of dielectric relaxation, and dipolar noise in polymer glasses. The dynamics and evolution of individual CRR was studied. Surprisingly, individual CRR were found to revisit a handful (2-4) of configurations up to hundreds of times. Statistical analysis of the noise gives information about the lifetime of the CRR, the local shape and evolution of the energy landscape, and the evolution from exponential to nonexponential response within a CRR.

PHYS 108 [659300]: Dynamically selective heating in viscous liquids

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Polar liquids are associated with dielectric loss which results in energy dissipation if exposed to a large amplitude sinusoidal electric field. We employ model calculations using the dielectric and calorimetric properties of supercooled glycerol in order to demonstrate that the effect of electric field heating is measurable under realistic conditions. In particular, the dynamically heterogeneous character of viscous liquids leads to an increase in the effective temperature of only those domains whose relaxation time matches the frequency of the electric 'burn field'. These computational results are compared with dielectric hole-burning measurements on supercooled glycerol across a large range of burn frequencies. The agreement between model and experiment demonstrates that fast and slow relaxations are independent (most likely spatially separated) and correlated with the time scale of the respective heat capacity contributions. The picture is consistent with frequency resolved heat capacity data on glycerol. It is argued that dielectric hole-burning effects can be rationalized on the basis of dynamically selective heating, where the local dipole temperature and the phonon bath temperature are only weakly coupled.