

# DIVISION OF PHYSICAL CHEMISTRY

**Final Program, 226th ACS National Meeting, New York, NY, September 7-11, 2003**

## **Sunday Program**

### Abstracts

#### **PHYS 1 [654598]: De novo design of peptides, proteins, and peptide mimetics**

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Our group has developed computational and synthetic methods for understanding the structural bases for protein function. In order to test some of the rules and concepts that are believed to be important for protein folding and stability we have designed several simple proteins that fold into predetermined three-dimensional structures. A number of helical bundle motifs have been designed, and structurally characterized to determine the features that are important for folding into a native-like structure. Further, the sequences of the designed helical bundles have been elaborated to introduce binding sites for small ligands and metal ions, including a diiron cluster similar to that observed in enzymes such as the R2 subunit of ribonucleotide reductase R2 E.coli and methane monooxygenase. We have also investigated the features required for folding and assembly of membrane proteins.

In a similar vein, we have designed non-peptidic oligomers that mimic the structures and biological properties of helical peptides that interact with phospholipid bilayers (e.g., antimicrobial peptides such as magainin), as well as helices that engage in protein-protein interactions.

#### **PHYS 2 [634970]: Combinatorial associations of the human bZIP transcription factor leucine zippers**

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The sequencing of the human genome has revealed approximately 55 human bZIP transcription factors that can form homo- or heterodimers to regulate a wide variety of biological processes. The information necessary for dimerization specificity is encoded in the coiled-coil or "leucine-zipper" domains of these proteins. We have used protein microarrays to carry out a comprehensive analysis of the intrinsic interaction specificity of the bZIPs. By paying particular attention to issues such as purity, valency and oxidation state, we have obtained very high quality interaction data, as judged by reproducibility, symmetry and agreement with solution studies. Our measurements of over 1400 unique pairwise combinations show that bZIP interactions are sparse and highly-selective in vitro. The resulting data provide an excellent foundation for a computational study of sequence and structural features that are responsible for interaction specificity.

#### **PHYS 3 [635265]: Structures and functions of de novo proteins from designed combinatorial libraries**

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Combinatorial libraries of de novo amino acid sequences can provide a rich source of diversity for the discovery of novel proteins. Randomly generated sequences, however, rarely fold into well-ordered protein-like structures. To enhance the quality of a library, diversity must be focused into regions of sequence space consistent with well-folded structures. We have designed focused libraries of sequences by constraining the binary pattern of polar and nonpolar amino acids to favor structures that contain abundant secondary structure, while simultaneously burying hydrophobic side chains in the protein interior and exposing hydrophilic side chains to the surrounding solvent. The

experimentally determined solution structure of a novel 102-residue protein from a binary patterned library is a four-helix bundle, as specified by the design. These results show that amino acid sequences that have neither been selected by evolution, nor isolated via high-throughput screening, nor designed by computer can form native-like protein structures. The implications and applications of these de novo proteins will be discussed as they pertain to molecular evolution, protein folding, 3-dimensional structure (alpha-helical and beta-sheet), cofactor binding, enzymatic catalysis, biosensors, amyloid formation, self-assembly, and biomaterials.

**PHYS 4 [654599]: A dynamic combinatorial library approach to protein design**

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For a given structural archetype, what amino-acid sequences define the most stable topologies?

Exchange-labile transition metal complexes of peptides augmented with appropriate metal-ion binding residues allow the thermodynamically controlled self-assembly of stable peptide oligomers which exhibit many of the biophysical properties characteristic of natural proteins.

Preliminary experiments clearly show that the folding free energy is coupled to metal-ion binding in the assembly of peptide helix dimeric and trimeric coiled coils. This coupling has been exploited to search for optimally stable sequence variants in virtual combinatorial libraries of over 200 million members.

Interrogation of the library using ion-cyclotron FT mass spectrometry permits stepwise dissociation of peptides from the oligomeric complexes, and subsequent sequencing. This allows us to definitively answer the question posed above.

**PHYS 5 [662755]: Directed evolution of proteins**

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*Abstract text not available.*

**PHYS 6 [635245]: Reactivity patterns of cytochrome P450 in oxygen transfer reactions: The protein, the active species and the chameleon**

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The active species of the cytochrome P450 enzyme is a high-valent iron-oxo species, so-called Compound I (Cpd I). I shall show that Cpd I behaves like a chameleon species that adopts its geometry and electronic structure to the protein environment in which it is accommodated, and that it changes its reactivity and selectivity patterns under the influence of hydrogen bonding and polarization effects, which mimic the protein environment [Schöneboom, et al. J. Am. Chem. Soc., 124, 8142-8151 (2002); De Visser, et al. Angew. Chem. Int. Ed., 41, 1947-1951 (2002)]. Using a chameleon species in many different protein environments is one of the ways by which the enzyme modulates its selectivity. The Chameleon oxidant can serve as a new paradigm in enzyme catalysis.

**PHYS 7 [637303]: Modeling chemical reactions in proteins by the QM/MM method based on the flexible effective fragment potential technique**

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Development and applications of a new approach to hybrid quantum mechanical - molecular mechanical (QM/MM) method, which is based on the effective fragment potential (EFP) technique (M.Gordon et al., J.Phys.Chem.A, 2001, 105, 293), are presented. Compared to the original formulation of the EFP theory, we introduce flexible chains of small EFs and replace EFP-EFP interactions by the MM force fields. The concept of effective fragments is also utilized to solve the QM/MM boundary problem across covalent bonds. The main emphasis of this approach is on

modeling chemical reactions in protein environments. Parameters of effective fragments corresponding to the principal units of aminoacids can be obtained in preliminary ab initio calculations. The applications include modeling chemical transformations for the serine protease enzymatic reaction, proton transfer over chains of water molecules in ion channels, hydrolysis of guanosine triphosphate by the Ras-GAP protein complex.

**PHYS 8 [643307]: Simulation of chemical reactions in enzymes with a density functional theory QM/MM free energy method**

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The density functional theory QM/MM free energy method for simulation of chemical reactions in enzymes will be presented. The method features (1) a pseudo-bond QM/MM approach to a smooth interface between the QM and MM regions, (2) an efficient iterative optimization method to determine optimized structures, (3) an efficient search of minimum energy paths for a system with thousands of atoms on the QM/MM potential and (4) a free energy perturbation approach to calculate the potential of mean force along the reaction path. Recent applications and comparison with experimental studies will be presented.

**PHYS 9 [639538]: Heterolytic OH bond breaking in the condensed phase: prediction of carboxyl pKa's in proteins using QM**

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A computational methodology for protein pKa predictions, based on ab initio quantum mechanical treatment of part of the protein and linear Poisson-Boltzmann equation treatment of the bulk solvent, is presented. The method is used to predict and interpret the pKa's of the five carboxyl residues (Asp7, Glu10, Glu19, Asp27, and Glu43) in the serine protease inhibitor turkey ovomucoid third domain. All the predicted pKa values are within 0.5 pH units of experiment, with a root mean square deviation of 0.31 pH units. We show that the pKa lowering observed for some of the residues is primarily due to hydrogen bonds (HBs) to the carboxyl oxygens. HBs involving amide protons are shown to be particularly important, and the effect of H-bonding is shown to be non-additive. Hydrophobic effects are also shown to be important in raising the pKa. Interactions with charged residues are shown to have relatively little effect on the carboxyl pKa's in this protein, in general agreement with experiment.

**PHYS 10 [643146]: The floating occupation molecular orbital reparameterized semiempirical configuration interaction method: Direct photodynamics for large chromophores in proteins and condensed phases**

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First principles simulations of photodynamics have recently been demonstrated using the ab initio multiple spawning (AIMS) method. The AIMS method uses a multireference wavefunction ansatz in order to achieve a globally accurate description of the ground and excited state potential energy surfaces and their nonadiabatic couplings. AIMS has been applied to molecules with up to 26 atoms; however, the extreme computational expense poses a serious obstacle to studies of large molecules and complex environments. We describe a floating occupation molecular orbital (FOMO) semiempirical configuration interaction (CI) method which ameliorates these difficulties and demonstrate its utility for photoactive protein dynamics. Electronic orbitals in the FOMO approach are determined by optimizing an ensemble energy using fractional (floating) occupation numbers within the framework of conventional SCF procedures. These orbitals are used in a subsequent CI expansion which describes the pure states. A complete active space (CAS-CI) expansion is generally chosen, although this is not essential. The floating occupation technique ensures the correct orbital degeneracy when needed, for example in case of dissociation processes or metal-containing molecules. Virtual orbitals are partially occupied and variationally optimized, enhancing convergence of the subsequent CI expansion. The FOMO method may be applied in the context of semiempirical or ab initio wavefunctions. Because semiempirical methods were not extensively parameterized for

excited states, reoptimization of the semiempirical parameters based on high quality ab initio or experimental data is often necessary when they are chosen. The FOMO-CASCI method has been incorporated in MOPAC, including the possibility of a hybrid quantum mechanical/molecular mechanical (QM/MM) description. Using the QM/MM decomposition, we treat the chromophore and possibly a small part of the environment using the FOMO-CASCI method. The remainder of the system is modeled with a classical force field method. Furthermore, we have incorporated the FOMO-CASCI-QM/MM method with direct nonadiabatic dynamics techniques, including both surface hopping and multiple spawning. The new FOMO-CASCI-QM/MM method is applied to the photodynamics of the Green Fluorescent Protein fluorophore in vacuum, aqueous, and protein environments. The results allow us to understand why the fluorophore exhibits its peculiar fluorescence only when embedded in the protein environment.

**PHYS 11 [639588]: Flow-induced crystallization precursors in polymer melt**

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In-situ SAXS (small angle X-ray scattering) and -WAXD (wide angle X-ray diffraction) techniques were used to probe the flow-induced crystallization precursor structures in polymer melt subjected to a shear field (in a parallel plate rheometer) as well as an elongational flow field (in a fiber-spinning equipment). The results of both shear and elongational flow studies suggest that a stable scaffold (or network) of primary nuclei, consisting of microfibrillar structures along the flow direction (form first) superimposed by layered structures perpendicular to the flow direction (form second), is generated in polymer melt prior to crystallization. Also, the investigation of the effects of shear rate and shear duration reveal that while the shear rate is more significant than shear duration, both shear rate and shear duration have pronounced independent effects on oriented structures development. Thus, not only the total strain but chosen combination of the rate and duration are important.

**PHYS 12 [644236]: Role of melt dynamics in flow-induced formation of oriented nuclei in polymer crystallization**

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Molecular aspects of polymer melt rheology play an extremely strong role in governing the processing–structure–property relations of semicrystalline polymers, the dominant materials in the plastics industry. Recent advances in experimental apparatus and methods have revealed that the dramatic changes in crystallization kinetics and morphology induced during shear follow a kinetic pathway. The rate of formation of oriented precursors is not limited by the usual activation barrier to nucleation, but instead occurs many orders of magnitude faster, at a rate that tracks the dynamics of the polymer chains in the melt. Model polymers and their binary blends have shown that the specific melt dynamics that control formation of the oriented threadlike nuclei ("shish") are those of the longest chains in the melt. The effect of the long chains is cooperative, greatly enhanced by long chain–long chain overlap. An adequate separation of relaxation times is required: "long chains" must be ~4.5-fold longer than average to enhance the transition to oriented crystallization, suggesting that chain stretching during shear mediates the propagation of threadlike precursors.

**PHYS 13 [668630]: Metastable phases and the nature of the melt state in polymer melts**

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Polymer crystallization continues to hold strong technological and academic interests. Crystallization from the melt is driven by a combination of the tendency of polymeric molecules to stiffen upon cooling, and the short-range attraction that drives crystallization in ordinary liquids. Recent studies have suggested that the appearance of the long-range crystalline state could be preceded, or even initiated, by density fluctuations distinct from those driven by the simple short-range monomer-monomer attraction. In this work we focus on the development of conformational order, or stiffening, in cooled polymer melts, and the different liquid-crystalline mechanisms by which density can

be implicated in this process. I will also discuss recent experiments on shear-induced crystallization, which provides an additional window into this behavior.

**PHYS 14 [642855]: Does conventional nucleation occur during liquid-liquid phase separation in polymer mixtures?**

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The initial stages of liquid-liquid phase separation in a metastable blend of high molecular weight polyolefins was studied by time-resolved neutron scattering. The large size of the polymer molecules causes chain entanglement to occur, leading to extremely slow dynamics. This enables direct examination of the initial clustering of molecules prior to macroscopic phase separation. We find that the scattering profiles are time-independent for scattering vectors larger than a critical scattering vector. We demonstrate the relationship between the lower cut-off for the size of the growing clusters ( $R$ ) and the critical scattering vector.  $R$  can be interpreted as the size of the critical nucleus. The dependence of  $R$  on quench depth is in qualitative disagreement with all known theories of phase separation kinetics. In particular we find no change in the dependence of  $R$  on quench depth upon crossing the spinodal. Our experiments suggest that the meaning of the conventional binodal and spinodal curves in polymer blend phase diagrams need reexamination. Recently, we have conducted two-step quenches into the metastable region of the phase diagram. The effect of the first step on growth kinetics observed during the second step was investigated. The results of these experiments will be discussed.

**PHYS 15 [669870]: Kinetics of individual grain growth in block copolymer order-order transitions**

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Polarized optical microscopy is used to follow the growth of individual grains in block copolymer solutions undergoing thermally induced order-order transitions. Of particular interest is the emergence of the gyroid phase (a bicontinuous cubic morphology) from disordered and cylindrical phases. In most cases this involves an intermediate metastable perforated layer state. Six different solutions of styrene-isoprene diblock copolymers were examined. In all cases the gyroid phase grows isotropically at a constant velocity. The growth velocity is a strong function of temperature and solution concentration, and varies over several orders of magnitude. The results compare quite favorably with the theory of Goveas and Milner.

**PHYS 16 [644588]: Dynamics versus length scales in hydrophilic A-B-A triblock copolymers**

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Ethylene oxide-propylene oxide-ethylene oxide triblock copolymers (PEO-PPO-PEO) are excellent models for studying the relations between structure and dynamics that occur over a broad range of aqueous solution phases. For a given sample of these triblock copolymer solutions, one can obtain random coil, variable size micelle, clusters, and gel phases solely by varying the temperature. We have used fluorescence probes of widely varying hydrophobicity to independently characterize both the hydrophilic and hydrophobic regions of the amphiphilic triblock copolymer solutions. Lifetimes, polarization anisotropies, and time-dependent fluorescence Stokes shifts experiments using coumarin 343-/Na<sup>+</sup> probe the hydrophilic water-PEO interactions, and consistently show solution-like dynamics. The same experiments using coumarin 153 probe the hydrophobic PPO regions, and show dramatic deviations in dynamics. Most interesting is the fact that the dynamics are changing most extremely at a temperature 20 degrees below the macroscopic gelation temperature, likely resulting from a drying transition occurring in the hydrophobic region.

**PHYS 17 [654994]: Clusters, facets and edges: Site-dependent selective chemistry on model catalysts**  
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No abstract available.

**PHYS 18 [639176]: Size selected metal clusters on surfaces and in the gas phase**  
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A new source has been developed for generating broad distributions of metal clusters with  $n$  up to about 100. These clusters can be mass selected and gently deposited on semiconductor surfaces under ultra high vacuum conditions. Preliminary results for a range of sizes of silver and gold clusters deposited on TiO<sub>2</sub> will be given, where characterization is done using high resolution STM/AFM analysis. Results will also be given for gas phase reactions of smaller coinage metal clusters reacting with propene, ethylene, oxygen and other ligands. Ligand induced fragmentation is induced in some systems and mechanisms will be given. Where possible equilibrium constants are measured as a function of temperature in order to obtain thermochemical quantities. High level ab initio calculations are done on all systems for comparison with experiment.

**PHYS 19 [655052]: Anionic gold clusters, and their reactivity**  
**Vladimir E. Bondybey**, I. Balteanu, O. P. Balaj, B. S. Fox, M. K. Beyer, and Z. Bastl, Technical University of Munich, Lichtenbergstrasse 4, D-85747 Garching, Germany

Reactions of size selected anionic gold clusters with CO and O<sub>2</sub> were investigated using Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy (FT-ICR MS). The clusters display an amazing variety and selectivity in their chemistry, with clusters of different sizes differing not only in terms of their reaction rates, but also in the reaction pathways, sequence and chemical behavior. The bimolecular CO adsorption on the gold clusters exhibits in general very low reaction rates, with overall, odd clusters reacting faster than the even species. On the other hand, the even clusters seem to exhibit higher propensity towards reaction with O<sub>2</sub>. Interesting sequential absorptions, ligand exchanges, and cooperativity effects between the adsorption of CO and O<sub>2</sub> are observed. No clear evidence for oxydation of CO is detected. The implication of the observations for the catalytic activity of gold will be discussed.

**PHYS 20 [643632]: Gas-phase transition metal cluster catalysis: Energetics of reaction intermediates**  
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Palladium and gold clusters catalyze the oxidation of CO to CO<sub>2</sub>. Guided ion beam tandem mass spectrometry techniques are employed to investigate the reactivity of small gas-phase metal cluster anions. The energetics of intermediates along the catalytic reaction path are examined by synthesizing beams of the clusters anions with adsorbed CO, O<sub>2</sub>, or CO<sub>2</sub> molecules, or O atoms. Energy-resolved collision-induced dissociation of these intermediate species allows determination of the threshold energies for desorption. The reactivity and energetics of the gas-phase palladium and gold cluster anions are compared with previous work on platinum clusters, and with the reactions on bulk surfaces and supported clusters. Issues of the efficiency of gas-phase catalysis are considered.

**PHYS 21 [644138]: Catalytic water formation on free platinum clusters**  
**Mats Andersson**, and Arne Rosén, Department of Experimental Physics, Chalmers University of Technology and Göteborg University, SE-41296 Göteborg, Sweden, Fax: 46-31-7723496, mats.andersson@fy.chalmers.se

A pulsed beam of platinum clusters is generated with a laser vaporization source. The cluster beam passes through two reaction cells and the clusters are detected with laser ionization and time-of-flight mass spectrometry. By measuring the abundance of pure clusters and reaction products as a function of reaction cell pressure, the reaction

probability in a cluster-molecule collision can be determined. The reaction probability of  $Pt_n$  ( $n=7-30$ ) with oxygen is for most sizes between 0.2 and 0.3, and appears somewhat lower with hydrogen (deuterium). When the clusters first react with oxygen and then with hydrogen the number of oxygen atoms adsorbed on the clusters decreases as the number of cluster-hydrogen collisions increases. The only reasonable explanation for this is that water molecules form on the clusters and desorb. The efficiency of the reaction is high on the cluster sizes investigated (7-30 atoms), with only a weak size dependence.

**PHYS 22 [644298]: Gas-phase molybdenum carbide and sulfide clusters and nanocrystallites: Production and reactivity**

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We are investigating the reactivity of molybdenum carbide and sulfide nanoparticles generated in the gas-phase. In the bulk,  $MoS_2$  is widely used as a catalyst for hydrodesulfurization and molybdenum carbide surfaces have been shown to be effective for promoting reactions involving C-H bond activation. The wider range of stoichiometries and particle structures afforded by nanoparticle synthesis is expected to provide a means to further tailor their activity. We have recently used a laser ablation plasma source to generate gas-phase  $Mo_mX_n$  ( $X=C, S$ ) clusters and nanocrystallites and are currently developing an ion beam apparatus to study size-selected free and deposited ions of the same material. Preliminary mass spectroscopy results show the production of a wide range of nanoparticle stoichiometries slightly different from those observed using laser ablation. The most recent data from this apparatus will be presented along with results from our laser ablation studies. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract No. DE-AC02--98CH10886

**PHYS 23 [636846]: Structural signatures of vitrification in hard core fluids**

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Free volume models suggest that the glass transition of a supercooled liquid occurs when the amount of unoccupied space becomes critically small. While several methods exist for quantifying local free volume, they have found limited application in describing the glass transition. Here, computer simulations of hard spheres and disks are used to estimate the most probable cavity size,  $\square_{cavity}$ , and a "rattle" size,  $\square_{rattle}$ , over which a particle can translate holding all other particles fixed. Both of these measures appear to extrapolate to zero at the random close packed density,  $\rho_{rcp}$ , close to the density where extrapolations of the viscosity diverge. We also identify the onset of caging by locating the density at which spontaneous void formation in the fluid is no longer a random event, but rather is localized to the immediate vicinity of existing cavities. These results suggest that vitrification can be viewed as a geometrical phenomenon, and that *local* free volume measures can identify the location of the onset of liquid-like dynamics, the complex dynamics of caged liquids, and vitrification.

**PHYS 24 [644487]: Particle rearrangements due to transitions between inherent structures of a supercooled Lennard-Jones liquid**

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Observing transitions between inherent structures near the mode-coupling temperature  $T_{MCT}$ , we quantify the displacements of individual particles, the localization of the rearrangements and the relevance of cooperative string-like motions. We find that all studied quantities vary smoothly through  $T_{MCT}$ . When the organization of the inherent structures into metabasins is considered, comparable features are observed for transitions inside and outside of

metabasins. Constructing sequences of transitions that connect different metabasins, we find that the particle displacements during subsequent metabasin transitions are uncorrelated. To study the mechanism of the string-like motion, we consider suitable sequences inside and outside of metabasins, respectively. In both cases, most strings do not move coherently during a single transition, but subunits of the strings are active at different times. We discuss the relation between the properties of the energy landscape and the relaxation processes in supercooled liquids.

**PHYS 25 [641881]: Density of states simulation of the thermodynamic and mechanical properties of glass formers. Bulk and confined systems**

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A novel method has been developed for simulation of glass forming systems. The method relies on a self-consistent estimate of the density of states, which is determined from knowledge of the instantaneous temperature of the system. Results for model glass formers consisting of binary mixtures of Lennard-Jones particles agree with literature results from molecular dynamics simulations. It appears, however, that the proposed method is able to sample configuration space at temperatures significantly lower than the mode-coupling temperature of the systems of interest. This new method is then used to probe the thermodynamic and mechanical properties of a variety of glassy systems. An analysis in terms of local moduli reveals that glassy materials can be mechanically inhomogeneous, and suggests that the dynamics of glasses are related to such inhomogeneities.

**PHYS 26 [632966]: Equilibration and frequency dependence of the specific heat of glass forming liquids**

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We show that a glass transition, signaled by a peak in the specific heat vs. temperature, can occur because a glassy system that shows no signs of aging progresses so slowly through the energy landscape that the time needed to obtain an accurate estimate of the thermodynamic averages exceeds the observation time. We find that below the glass transition temperature of a three dimensional binary mixture of soft spheres, the specific heat increases with measurement time spans orders of magnitude longer than previously recognized equilibration times such as the alpha relaxation time and the aging time. The specific heat displays frequency dependence down to correspondingly low frequencies.

**PHYS 27 [643902]: Low temperature properties of glass forming liquids from computer simulations**

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Most computer simulation studies of dynamic and thermodynamic behaviour of glass forming liquids to date have been confined to temperatures above the mode coupling temperatures because of the large relaxation times involved in simulating liquids at lower temperature. However, it is beginning to be possible to study the behaviour below the mode coupling temperature with present day computers. Results are presented concerning the dynamic and thermodynamic behaviour of model glass forming liquids near and below the mode coupling temperature, including the observed change in qualitative behaviour below the mode coupling temperature, and results pertaining to the existence of an ideal glass transition.

**PHYS 28 [637278]: Understanding the dynamics of a supercooled liquid in terms of its potential energy landscape**

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The jump motion among potential energy minima of a Lennard-Jones model glass former is investigated by extensive computer simulations. From the time series of minima energies one can identify a superstructure of the energy landscape giving rise to the notion of metabasins. The long-range dynamics can be described as a random-

walk among metabasins. This is reminiscent of a trapping picture. The whole temperature dependence is contained in the distribution of waiting times. Furthermore it is possible to define an effective activation energy to leave a metabasin of given depth. These activation energies result (i) from a direct analysis of the dynamics and (ii) from a quantitative analysis of the relevant reaction paths. In this framework it is possible to predict the temperature dependent diffusion constant from knowledge of the distribution of metabasins (thermodynamics) and the effective activation energies. Implications and possible applications of these results are discussed.

**PHYS 29 [644513]: Protein optimization with high throughput virtual and experimental screening**

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Many naturally occurring proteins have potentially powerful applications, but require modulation or optimization of their properties for use. Recently developed tools for structure-based protein design are being used to improve these proteins and increase their value. We use proprietary structure-based design tools such as Protein Design Automation® technology to pre-screen vast numbers of protein sequences in silico. By screening enormous diversity computationally, low fitness sequences are eliminated from consideration and highly focused sequence libraries are created for experimental screening. These libraries facilitate the rapid discovery of improved proteins with very efficient use of experimental resources. In silico library generation finds protein sequences that are completely novel by screening the full diversity of protein sequence space. This technology has been applied to numerous systems including important industrial and pharmaceutical proteins and has a demonstrated record of success.

**PHYS 30 [654589]: Grid computing methods for enhancing sampling and accuracy in computational protein design**

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One of the greatest challenges in computational protein design is the balancing of the use of accurate (but computationally expensive) models with sufficient sampling in sequence space. By using a grid computing resource of tens of thousands of CPUs, we have performed extensive sequence space sampling using state of the art models, leading to very large-scale design libraries. Our results indicate the degree of sampling (library size) needed and suggest how one can better balance the needs of sampling and accuracy. Finally, we apply our design libraries to other problems, such as the design of novel function and to the structure prediction problem.

**PHYS 31 [641850]: Ab initio profile for a given backbone structure - application to protein design and the detection functionally important residues**

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We have developed a method based on a self-consistent statistical theory to calculate amino acid probabilities of sequences (i.e., an “ab initio” profile) consistent with a particular backbone structure. The method quantifies amino acid variability at each residue site from a physico-chemical point of view. These results may be compared with multiple sequence alignments of homologous sequences produced during the course of evolution. For a variety of protein structures, comparison of ab initio and evolutionary profiles shows that they are significantly consistent with each other at about half of the residue sites. Significant discrepancy of the profiles is often found at biologically functional sites, suggesting the potential use of this comparison for predicting functionally important residues. In protein design, the profile information can be used to direct the synthesis of particular sequences as well as to identify the range of amino acid variability at selected sites. Such information may be used to engineer functional sites into proteins.

**PHYS 32 [642407]: Computational approaches for combinatorial protein library prescreening and optimization**

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Combinatorial protein library generation and screening has emerged as a powerful strategy for protein engineering. We present methods for identifying and reducing the fraction of reassembled sequences with diminished functionality due to unfavorable "clashing" interactions between protein fragments. First, a rapid prescreen for identifying residue-residue clashes is presented that considers: introduction of repulsive pairs (+/+ or -/-), disruption of H-bonds, and generation of steric clashes or cavities. Second, mean-field theory calculations are performed on a structure-based computational model to further evaluate the plasticity of residue-residue substitution patterns. With these two methods, we found that crossovers are preferentially distributed to avoid the formation of clashes in the hybrids. Lastly, an optimization framework is introduced for redesigning clashes, either upstream in the parental sequences or downstream in promising hybrids. A deterministic algorithm for the rotamer optimization problem that combines dead-end elimination with an integer programming model is presented.

**PHYS 33 [631431]: Modeling reactive chemistry in protein active sites via mixed quantum mechanics/molecular mechanics methods**

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We have developed mixed quantum mechanics/molecular mechanics (QM/MM) methods specifically designed to model reactive chemistry in protein active sites. The methodology will briefly be reviewed, followed by applications, using ab initio DFT methods for the QM region, to a wide range of proteins including methane monooxygenase, cytochrome P450, and triose phosphate isomerase. Quantitative agreement with experiment for structures, thermodynamics, and kinetics will be emphasized; typical errors obtained to date over a wide range of systems are on the order of a few kcal/mole.

**PHYS 34 [644669]: Reactions of relevance to biological systems**

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*Abstract text not available.*

**PHYS 35 [637261]: Bond breaking and bond making in photobiology: Structure of the excited state force field of retinal chromophores**

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Computational studies on different models of the 11-cis retinal chromophore (PSB11) of rhodopsin (i.e. the human retina visual pigment) indicate that a correct description of the geometrical and electronic structure of these chromophores can be achieved using an ab initio CASPT2//CASSCF/6-31G\* level of theory (i.e. CASSCF geometry optimization and CASPT2 energy evaluation). Here we show that the same strategy can be used to investigate the factors responsible for the ca. 150 fs excited state (S1) lifetime observed in rhodopsin. Indeed, comparison of the S1 reaction path for the native chromophore and: (1) reduced chromophores, (2) locked chromophores and (3) counterion-chromophore pairs, give an unprecedented description of the sensitivity of retinal to intramolecular and environmental factors. Most importantly, we show that the QM/MM scheme CASPT2//CASSCF/AMBER allows for the evaluation of the equilibrium structure and excited-state properties and relaxation in the protein environment.



**PHYS 36 [644201]: Solvation dynamics in protein environments**

**Xueyu Song**, Primit Chowdhury, Mintu Halder, and Jacob W. Petrich, Department of Chemistry, Iowa State University, Ames, IA 50011, Fax: 515-294-0105, xsong@iastate.edu

A simple inhomogeneous model of protein dielectric properties will be discussed. A protein in solution is modelled as a collection of polarizable dipoles in a cavity embedded inside a dielectric medium. The intrinsic polarizabilities of 20 amino acids are assumed to be portable to all proteins in nature. A reasonable set of these polarizability values has been obtained by comparing dielectric fluctuations from molecular dynamics simulations with model calculations. The results are consistent within a data set of three small proteins. In order to validate the model ultra-fast laser spectroscopy experiments are performed for a chromophore in various mutants of myoglobin. The comparison between theory and experiments will be discussed.

**PHYS 37 [644663]: Development of nonadiabatic molecular theory for simultaneous determination of nuclear and electronic wave functions: ab initio NOMO theory**

**Hiromi Nakai**, Department of Chemistry, Rice University, 6100 South Main, MS-60, Houston, TX 77005-1892, nakai@waseda.jp

We have developed a simultaneous determination method of nuclear and electronic wave functions without the Born-Oppenheimer (BO) approximation, which is termed as ab initio NOMO theory. The Hartree-Fock (HF) equations have been derived for the nuclear orbital (NO), which is one-nucleus wave function, and the electronic molecular orbital (MO). Many-body effects have been examined and found that the electron-nucleus correlations are very important in our treatment. The separation of vibrational motion from the translational and rotational ones is also important in case adopting the Gaussian basis functions for the NOs. To represent the vibrational and electronic excited states, we applied the configuration interaction (CI) method to the NOMO theory.

**PHYS 38 [641335]: Viscosity of monolayers at coexistence**

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The primary function of lung surfactant (LS) is to form a monolayer at the alveolar air/water interface capable of lowering the surface tension to near zero values. An important corollary to this is that the monolayer must also be able to resist collapse upon the compression that accompanies expiration. One role of the lung surfactant specific proteins SP-B and SP-C is to stabilize the monolayer against collapse; the collapse structure of monolayers with SP-B or SP-C are dramatically different from that without lung surfactant proteins. These novel collapse structures are likely due to changes in the mechanical properties of the monolayer induced by the proteins. We use a magnetic needle viscometer along with optical and probe microscopy to study synthetic lung surfactant systems to determine the relationship between lung surfactant components and monolayer mechanical properties. Systematic measurements of monolayer viscosity as function of protein concentration, temperature, and phase behavior are reported and their relations to three dimensional suspensions of hard spheres are discussed. The proteins appear to act to modulate the relative proportions of liquid and solid phases at coexistence, which determines the monolayer viscosity.

**PHYS 39 [632652]: Seeing spots: miscibility transitions in lipid/cholesterol membranes**

**Sarah L. Keller**, Sarah L. Veatch, and Benjamin L. Stottrup, Departments of Chemistry and Physics, University of Washington, Campus Box 351700, Seattle, WA 98195-1700, Fax: 206-685-8665

Mammalian cells are surrounded by an outer wall or "plasma membrane" of proteins and lipids arranged in opposing leaflets of a bilayer. There is growing evidence that this membrane is not uniform, but instead laterally separates into different liquid phases. We study lateral phase separation in model experimental systems of lipids. Using ternary mixtures of a saturated phospholipid, an unsaturated phospholipid, and cholesterol we observe coexisting liquid domains both in bilayers (in free floating giant unilamellar vesicles) and in monolayers (at an air-water interface). We find that the same lipid mixtures that produce liquid domains in bilayer membranes produce two upper

miscibility critical points in the phase diagrams of monolayers. We also find that it is possible to capture the monolayer domains on silanized glass substrates.

[S.L. Veatch and S.L. Keller, Organization in Lipid Membranes Containing Cholesterol, Phys. Rev. Lett. 89, 268101, 2002.]

#### PHYS 40 [644657]: Morphology and collapse of binary phospholipid monolayers

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Morphology and collapse in binary mixtures of saturated and unsaturated lipids have been studied at various temperatures using surface pressure-area isotherms and concurrent fluorescence microscopy. In particular, for Langmuir monolayers of a 7:3 mixture of DPPC (dipalmitoylphosphatidylcholine) and POPG (palmitoyloleoylphosphatidylglycerol) [J. Phys. Chem. B 2001, 105, 10348-10354] collapse above 33 °C is primarily by formation of vesicles and tubular structures from the parent film. Below 30 °C, however, the monolayer is biphasic at collapses and predominantly forms large-scale folds that reliably unfold upon expansion. In this and other mixtures, we show that the manner in which the monolayer, under compression, explores the third dimension at collapse correlates with the monolayer morphology prior to collapse. The reversible formation of folds at low surface tension is a potential model for Lung Surfactant function. A physical model based on statistical image analysis is presented herein to help elucidate this folding phenomenon.

#### PHYS 41 [644685]: Mechanism of peptide-induced lamellar to inverted hexagonal phase transition in phospholipid systems using coarse grain molecular dynamics

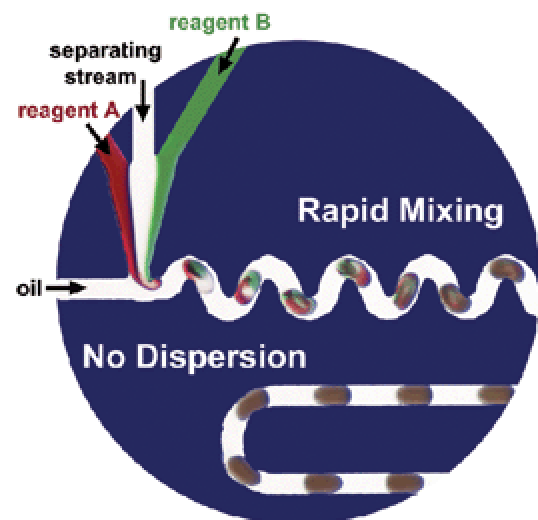
**Steve O. Nielsen**<sup>1</sup>, Carlos F. Lopez<sup>1</sup>, Preston B. Moore<sup>2</sup>, and Michael L. Klein<sup>3</sup>. (1) Department of Chemistry, Center for Molecular Modeling, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104-6323, Fax: 215-573-6233, snielsen@cmm.upenn.edu, (2) Department of the Sciences in Philadelphia, Department of Chemistry, (3) Department of Chemistry, University of Pennsylvania

The lamellar (bilayer) to inverted hexagonal phase transition in hydrated phospholipid systems can be induced either by heating or by the introduction of transmembrane peptides whose hydrophobic length is shorter than that of the bilayer. Heating has the effect of reducing the water to lipid ratio in the system. Molecular dynamics simulation results are presented in support of a proposed mechanism for the peptide-driven phase transition. This mechanism consists firstly of meniscus formation in the vicinity of the peptide which depletes the water layer in the adjacent regions. This local depletion can be significant enough to allow the membranes to fuse due to thermal fluctuations. The lipid head groups then rearrange to solvate the newly formed water pores, resulting in an inverted phase. At lower peptide concentrations, the phase transition is incomplete or does not occur.

#### PHYS 42 [641345]: Using microfluidics to control chemical systems in time

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We have developed a microfluidic system that can be used to control networks of chemical reactions in time. It uses fluid flow to convert spatial evolution of chemical systems into temporal evolution. Laminar streams of several aqueous solutions of reagents are injected into a hydrophobic channel with a flow of water-immiscible oil, where the aqueous solutions spontaneously form streams of plugs separated by oil. Each plug acts as a miniature reactor with a volume of ~ 200 pL that induces rapid (<1 ms) mixing by chaotic advection, and transports with no dispersion. This system has been validated by measuring single-turnover rate constant of RNase A. A complete reaction profile



with millisecond resolution was obtained from a spatially resolved image using <100 nL of solutions. This system will serve as a research tool for studying time-dependent processes -- especially those that involve complex networks -- in chemistry, biochemistry and biophysics.

**PHYS 43 [639948]: Microfluidic applications for nucleic acid and protein sizing**

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Microfluidic technology offers the benefits of miniaturization, integration, and automation that can lead to faster analysis with higher data quality and higher sample throughput. One of the first microfluidic systems commercialized is for biomolecular sizing using the principles of gel electrophoresis. In these chips, the microchannels are filled with a polymer solution at a concentration above the entanglement threshold. For DNA and RNA sizing, the procedures of sample injection, fluorescent dye staining of the analyte, electrophoretic separation by size, and optical detection of size fractions are integrated. These microchip analyses are similar to those performed in conventional capillary electrophoresis, except that the analysis times are usually an order of magnitude shorter. For protein sizing in sodium dodecyl sulphate (SDS) micelle solutions in which the proteins are denatured, an additional step of protein destaining is also integrated onto the chip, enabling an application that has no simple analog in conventional capillary electrophoresis. The scaling laws based on polymer physics considerations dictating the sizing mechanisms and separation efficiencies for these microfluidic applications will be discussed.

**PHYS 44 [632858]: Hydrocarbon reactions on oxide-supported metal nanoparticles**

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Oxide-supported metal catalysts have been studied here using well-defined surfaces involving vapor-deposited metal films on single-crystal oxides. Angle-resolved X-ray photoelectron spectroscopy (ARXPS), low-energy He<sup>+</sup> ion scattering spectroscopy (ISS), non-contact atomic force microscopy (nc-AFM), low-energy electron diffraction (LEED) and temperature programmed desorption (TPD) were used to characterize the resulting metal nanoparticles formed and their chemisorption properties toward hydrocarbons. The heats of adsorption of metal atoms on MgO(100), measured calorimetrically as a function of the resulting metal particle size, show a dependence on particle size that is much stronger than suggested by the Gibbs-Thompson relation. This strong dependence helps explain the observed strong variation in chemisorption properties with particle size. This result will be contrasted with the frequent observation of structural insensitivity in hydrocarbon dehydrogenation and hydrogenation reactions on metal particles. The reasons for this apparent discrepancy will be discussed. Work supported by NSF and DOE-OBES, Chemical Sciences Division.

**PHYS 45 [643861]: Chemistry and catalysis of metal clusters on surfaces**

**Ulrich Heiz**, Institute of Surface Chemistry and Catalysis, University of Ulm, Albert-Einstein-Allee 47, Ulm 89069, Germany, Fax: +49-731-5025452, ulrich.heiz@chemie.uni-ulm.de

The reactivity of nanoscale systems are mainly dominated by quantum-size effects that govern the electronic spectra of clusters, by the structural dynamical fluxionality of clusters, as well as by impurity-doping effects. In this talk these fundamental and unique cluster properties are illustrated by specific examples obtained from molecular beam experiments in the gas phase and experiments on size-selected clusters on surfaces. Where possible, concepts for their understanding are given. Specifically, the nanoscale reactivity of free, small metal clusters will be presented. It will be shown how the interaction and chemical reactivity can be changed with cluster size. On a specific example it will be shown how the reaction mechanism and the energetics of a catalytic cycle can be extracted from the measured, temperature-dependent kinetics. The experimental results are then compared to extensive ab-initio calculations. In a second set of experiments metal atoms and small metal clusters are formed in the gas phase, size-selected and then deposited on thin oxide films grown on metal surfaces. Chemical reactions and catalytic properties on the obtained cluster-assembled materials are then investigated under UHV conditions by means of thermal

desorption, infrared spectroscopy and pulsed molecular beams. The oxidation and polymerisation reactions are strongly dependent on cluster size and on the cluster-support interaction, and not only the number of product molecules per cluster is changed, but also the branching ratio of the certain reactions. In many cases the measured reactivities are different from the ones obtained for the corresponding bulk systems. By combining the obtained experimental results with ab-initio calculations, a picture of the size-dependent behavior of cluster-assembled materials is now emerging.

**PHYS 46 [662346]: Structural, electronic, and doping effects in nanocatalysis by supported and free gold clusters**

**Uzi Landman**, and Hannu Häkkinen, School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430

The unique properties of size-selected metal nano-clusters, underlie the remarkable newly found catalytic activity of small gold clusters (both when supported on metal oxide surfaces as well as in the gas-phase). These include: (i) structural dynamical fluxionality, (ii) quantum size effects reflected in size-dependence of the electronic energy-level spectra and charging characteristics, and (iii) impurity-doping effects that allow modification and control of the chemical reactivity. We discuss research efforts aimed at these “nanocatalytic factors” (see H. Hakkinen, et. al., *Angew. Chem. Int. Ed.* 42, 1297 (2003)), and illustrate them through joint experimental and theoretical investigations.

**PHYS 47 [633590]: Bond energies of molecular fragments to transition metal clusters**

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In this work, we examine the kinetic energy dependences of the reactions of  $\text{Fe}_n^+$  and  $\text{Ni}_n^+$  ( $n=2-15$ ) with  $\text{CD}_4$  and  $\text{ND}_3$  in a guided ion beam tandem mass spectrometer over the energy range of 0-10 eV. Metal cluster cations are formed in a laser vaporization/supersonic expansion source and reactions are performed under single collision conditions. The kinetic energy dependences are analyzed to determine thresholds for various primary and secondary reactions. From these thresholds, bond energies for iron and nickel cluster cation bonds to C, CD,  $\text{CD}_2$ ,  $\text{CD}_3$ , N, ND,  $\text{ND}_2$ , and  $\text{ND}_3$  are determined. For other atomic systems, bond energies to modest size metal clusters (10-15 atoms) reach bulk phase values. Thus, values for the molecular fragments provide some of the very FIRST data for the thermochemistry of such species bound to surfaces, information that is virtually non-existent even though these are key intermediates in a variety of catalytic processes.

**PHYS 48 [642352]: Surface scattering studies of gold nanocluster chemistry**

**Charles Buddie Mullins**, Department of Chemical Engineering, University of Texas, 1 University Station C0400, Austin, TX 78712-1062, Fax: 512-471 7060, mullins@che.utexas.edu

Gold nanoclusters supported on a titania single crystal are probed by molecular beam surface scattering methods in order to investigate their catalytic activity toward the carbon monoxide oxidation reaction. We typically populate the surface with adsorbed oxygen using a plasma-jet, radio-frequency powered oxygen source. Neat beams of CO are then impinged on the surface at various temperatures and oxygen coverages to test the oxidation reactivity. In particular, we will report on the reactivity of CO towards molecularly adsorbed oxygen as well as atomically adsorbed oxygen. We will also report on the effect of cluster size on oxidation activity over a temperature range from 77 - 400 K.

**PHYS 49 [670756]: Unified classical and quantum theory of structural glasses**

**Peter G. Wolynes**, Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, pwolynes@ucsd.edu

The relationship of glassy dynamics to an underlying random first order transition along with its accompanying entropic droplet excitations clarifies many puzzles in the phenomenology of structural glasses. I will discuss how this framework provides a quantitative treatment first of glassy phenomena in the classical regime: the coefficients in the

Vogel- Fulcher law, relaxational heterogeneity and the mesoscopic hydrodynamics of viscous liquids can be calculated without adjustable constants from thermodynamic data alone. The patterns of behavior associated with liquid "fragility" can all be traced to the magnitude of configurational heat capacity. Quantizing these droplet excitations greatly enriches the standard two level system model of low temperature glass properties. The quantum theory explains how the universal scaling of the low energy density of states with  $T_g$  arises, along with the peculiar universality of the phonon scattering mean free path in glasses. Deviations from the two level picture are predicted. These occur a higher temperature where they connect to the Boson peak and also occur at ultra low temperature where a gap in the density of state should arise.

**PHYS 50 [632616]: To move or not to move, and in what direction: The essentials of glass formers**

**David Chandler**, Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, Fax: 510-643-1566, [chandler@cchem.berkeley.edu](mailto:chandler@cchem.berkeley.edu), and **Juan P. Garrahan**, Department of Physics, University of Oxford

This lecture describes a coarse grained model for atomic glass formers. Its elements are physically motivated local microscopic rules for dynamics that are parameterized by observables. Quantitative results of the model are easily established and have been used to successfully interpret existing dynamic and thermodynamic experiments. Further testable predictions of the model will be discussed.

**PHYS 51 [670741]: Dynamic heterogeneities, defects, and the non-topographic view of glass transition phenomena**

**Juan P. Garrahan**, and Ludovic Berthier, Department of Physics, University of Oxford, 1 Keble Road, Oxford, OX1 3NP, United Kingdom, [j.garrahan1@physics.ox.ac.uk](mailto:j.garrahan1@physics.ox.ac.uk)

We show that most aspects of the dynamics of glass forming systems, including the dynamics between inherent structures (or dynamical traps) and the crossovers associated with the "landscape influenced" and "landscape dominated" regimes, can be understood in purely dynamical terms, without any reference to "topographic" features of the potential energy landscape. This "non-topographic" interpretation is based instead on the existence of dynamic heterogeneities and on their statistical properties. Our view is supported by the study of dynamically facilitated models of glass formers, which realize the excitation or defect picture of glass transition phenomena. This approach allows for the formulation of quantitative theoretical predictions which are successfully compared with numerical and experimental studies of local dynamics of supercooled liquids.

**PHYS 52 [631636]: Dynamics of elementary excitations in supercooled liquids: on the universality of relaxation time near the crossover temperature**

**Udayan Mohanty**, Department of Chemistry, Boston College, Chestnut Hill, Newton, MA 02467, Fax: 617-552-2705, [mohanty@bc.edu](mailto:mohanty@bc.edu)

We demonstrate a novel connection between fragility index and thermodynamic observable quantities in supercooled liquids. The predictions of the model are in good agreement with experimental data for supercooled organic and polymeric liquids. We show that recently observed universality of relaxation time near the crossover temperature is intricately governed in part by the equilibrium nature of the supercooled liquid. We then ask what these properties are and whether an elucidation of the thermodynamic route will provide insights into non-equilibrium factors. The latter is based on the idea that for supercooled liquids one can introduce dynamical variables that have characteristics of "elementary" excitations. The lifetime of the "elementary" excitations is determined by a variational technique. By imposing self-consistency between the lifetime of the "elementary" excitations and hopping relaxation time on the potential energy surface, the relaxation time near the crossover temperature is estimated. The predictions are critically compared with experimental data.

**PHYS 53 [644667]: Dynamic transition in glass-forming liquids and proteins**

**Alexei Sokolov**, Department of Polymer Science, The University of Akron, 170 University Ave., Akron, OH 44325, Fax: 330-972-5290, [alexei@uakron.edu](mailto:alexei@uakron.edu)

An overview of experimental results demonstrating qualitative changes in dynamics of glass forming systems at temperatures much above conventional glass transition,  $T_g$ , is presented. These results support the idea of existence of a crossover from liquid-like to solid-like dynamics on a molecular scale at some temperature  $T_D \sim 1.2-1.5 T_g$ . Analysis of great variety of small molecular and polymeric, ionic, hydrogen- and covalent-bonded glass-forming liquids reveals that the dynamic transition happens at some universal relaxation time  $\tau \sim 10^{-7}$  sec. Possible reasons for such a universal  $\tau$  are discussed.

We demonstrate that dynamics of proteins and DNA is very similar to dynamics of glass-forming liquids and also shows the dynamic transition. It is known that the dynamic transition in proteins can be shifted or completely suppressed by changing solvent. We demonstrate that the dynamic transition in proteins and DNA is controlled by the dynamic transition in the solvent. Thus proteins and DNA are “slaves” of solvents and that opens way to control their biochemical activity.

### **PHYS 54 [638498]: Glassy Kinetics in Protein Folding**

**Jin Wang**, Department of Chemistry, SUNY, Stony Brook, Stony Brook, NY 11794, jinwang@sprynet.com

Through the analysis of the kinetics of first passage time, population dynamics, and paths, the glassy nature of protein folding is explored. We found at a temperature between thermodynamic folding transition temperature and glass transition temperature, the kinetics experiences a transition from single exponential process to multiexponential process, and a power law behavior of the first passage time distribution starts to emerge from the Poisson or log-normal behavior. There is also a transition from multiple paths to discrete paths.