# SYMPOSIUM N

# Dynamics in Small Confining Systems VIII

November 28 - December 1, 2005

## Chairs

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\* Invited paper

**8:30 AM *N1.1**
**Atomic-scale Friction Experiments.** <u>Ernst Meyer</u>[1], Anisoara Socoliuc[1], Enrico Gnecco[1], Sabine Maier[1,2] and Roland Bennewitz[2]; [1]Department of Physics, University of Basel, Basel, BS, Switzerland; [2]Departmente of Physics, Mc Gill University, Montreal, Quebec, Canada.

The work presented in this paper is focussed on friction force microscopy under ultrahigh vacuum (UHV) conditions, which is an ideal tool to investigate small contacts. The normal force can be adjusted in the range from 0.1 to 100nN. Atomic-scale stick slip is observed on surfaces, such KBr(001) or NaCl(001). The velocity dependence of atomic-scale stick-slip shows a logarithmic increase. This logarithmic increase can be interpreted in terms of the Tomlinson model, when thermal activitation is included. At lower speeds the number for thermal activation events is increased, which leads to a reduced average frictional force. The dependence of friction as a function of normal force has been revisited recently. For small applied normal forces, a transition from atomic-stick slip to smooth sliding with minimum dissipation is observed. The results are found to be in reasonable agreement with the Tomlinson model, which predicts that instabilities disappear below a certain threshold. It is observed that the lateral contact stiffness does depend only weakly on the normal force. The experimental results are compared with simulations, where different tip geometries are investigated. A further increase of the loading can lead to the observation of another transition into the wear regime. Nanometer-scale modifications are produced and monitored by force microscopy.

**9:00 AM *N1.2**
**Superlubricity, Thermolubricity and Capillary Effects in Atomic-Scale Friction.** <u>Joost W. M. Frenken</u>[1], Martin Dienwiebel[2], Kochupurackal B. Jinesh[1] and Sergey Yu. Krylov[3]; [1]Kamerlingh Onnes Laboratory, Leiden University, Leiden, Netherlands; [2]IAVF Antriebstechnik AG, Karlsruhe, Germany; [3]Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russian Federation.

This talk highlights several surprises in atomic-scale friction measurements on graphite. We have constructed a special-purpose friction force microscope [1,2] with which we have investigated the lateral forces between a tungsten tip and a graphite surface as a function of normal force, relative orientation, sliding direction, scan speed, scan size, and relative humidity. At low humidity, we observe pronounced orientational effects, which provide strong evidence for orientational lubricity, also known as �assuperlubricity�assu [3-5]. The sliding is argued to take place between a graphite flake, firmly attached to the tungsten tip, and the graphite substrate. Based on a more quantitative analysis, it is further shown that thermal excitations dramatically lower the friction force, an effect that we refer to as �assthermolubricity� [6]. We propose that these two effects provide the reason for the excellent lubricating properties of graphite. When the humidity is deliberately increased, we measure the effects of capillary condensation of water between the tungsten tip and the graphite substrate. Depending on the humidity, the scan range and the scan speed, we find a variety of peculiar effects that indicate that the condensate behaves more like ice than like water [7]. [1] M. Dienwiebel et al., Rev. Sci. Instrum. 76 (2005) 043704. [2] T. Zijlstra et al., Sensors and Actuators A: Physical 84 (2000) 18. [3] M. Dienwiebel et al., Phys. Rev. Lett. 92 (2004) 126101. [4] M. Dienwiebel et al., Surf. Sci. 576 (2005) 197. [5] G.S. Verhoeven et al., Phys. Rev. B 70 (2004) 165418. [6] S.Yu. Krylov et al., Phys. Rev. E 71 (2005) 065101. [7] K.B. Jinesh et al., to be published.

**9:30 AM N1.3**
**Collective Pinning as a Mechanism for How Coatings of Hard Materials Can Reduce Friction between Solid Surfaces to Extremely Small Values.** <u>Jeffrey B. Sokoloff</u>, Physics, Northeastern University, Boston, Massachusetts.

In collective pinning theory, the problem of two three dimensional solids in contact is at its critical dimension. This implies that when the disordered stresses acting between the two solids at the interface are relatively strong compared to the elastic constants, the force of static friction should be large, but at smaller values of these forces, the system switches over to a regime of weak static friction. The possibility that this mechanism could provide a mechanism for how very stiff coatings are able to reduce friction to extremely low values is explored by taking into account the existence of roughness on several length scales.

**10:15 AM *N1.4**
**The response of monolayers and organic networks to stress as a function of molecular architecture: Applications in nanoscale tribology and patterning.** <u>Robert W. Carpick</u>[1], E. E. Flater[1], W. R. Ashurst[4], M. P. de Boer[2], H. T. Evensen[3], Hongquan Jiang[1], K. W. Gotrik[1] and F. S. Denes[1]; [1]University of Wisconsin - Madison, Madison, Wisconsin; [2]Sandia National Laboratories, Albuquerque, New Mexico; [3]University of Wisconsin - Platteville, Platteville, Wisconsin; [4]Auburn University, Auburn, Alabama.

The mechanical and tribological response of organic materials at small length scales is of critical interest to a wide range of applications, from nanoscale patterning to micro- and nano-scale machines. I will first discuss how self-assembled monolayers (SAM) respond to stress at the nanoscale, and in particular I will highlight studies of adhesion, friction, and stiffness of self-mated (i.e. SAM-on-SAM) interfaces a few nanometers in lateral dimension, as measured with atomic force microscopy (AFM). SAM coatings attached to silicon via silane or alkene head groups are applied to both the sample and the AFM tip. Consistent with previous studies of thiol SAMs, we observe an increase in friction with fluorination of the monolayer. Directly-attached alkenes also exhibit and increased friction with respect to silane-based films. Calibrated friction and lateral stiffness measurements are used to determine that the interfacial shear strength of the films exhibit significant but distinct pressure dependences. I will discuss how all of these differences are connected with the molecular architecture of the films. I will then discuss how stress can be used to generate sub-micron topographic patterns in cross-linked networks of polydimethylsiloxane (PDMS). The method is fast, inexpensive, and can be uniformly applied to macroscopically large areas in a single procedure. Exposure of pure spin-coated PDMS to an argon plasma leads to the formation of a siloxane network in the near-surface region, as confirmed by surface spectroscopy measurements. This silica-like surface layer is put into compressive stress when the sample cools after plasma exposure due to differential thermal contraction with the remainder of the film, generating a wrinkling pattern. The wavelength, amplitude, and pattern characteristics are controlled by modifying the plasma conditions, the initial PDMS film thickness, and the PDMS molecular weight. Atomic force microscopy is used to study the nano-scale topography as a function of these parameters. Comparison to a recent analytic model of wrinkling provides a theoretical framework for the results.

**10:45 AM N1.5**
**Mix Surfactant/Polymer Boundary Lubricant Films.**
<u>Carlos Alberto Drummond</u> and Philippe Richetti; Centre de Recherche Paul-Pascal CNRS, Pessac, France.

The normal interaction and the behavior under shear of mica surfaces covered by several surfactant, copolymers or surfactant-copolymer mixtures were studied by combining the capabilities of the Surface Forces Apparatus and the Atomic Force Microscopy. Several water-soluble surfactants with positively charged quaternary ammonium head-groups were investigated. These cationic surfactants spontaneously adsorb on the negatively charged mica surfaces from aqueous solution, the morphology of the adsorbed layer being determined by the molecular structure of a particular surfactant. This morphology has important implications on the behavior under shear and compression of the layer. When hemifusion of the adsorbed surfactant layers can be induced, the surfaces under shear show at least five distinctive dynamic regimes. The general behavior may be described by a model based on the kinetics of formation and rupture of adhesive bonds between the shearing surfaces. On the contrary, when hemifusion or removal of the adsorbed surfactant layers cannot be induced by shear and/or compression, no significant friction force can be measured. When a nonionic water-soluble copolymer is introduced in the solution it can co adsorb on the boundary layer. We observed that the behavior under shear, the adhesion energy and the resistance to hemifusion of the mix adsorbed layers are increasingly modified as the density of physigrafted copolymer molecules is augmented. These changes will be discussed in detail.

**11:00 AM *N1.6**
**Dissipative mechanics of thin fluid and polymer films.**
<u>John Pethica</u>, CRANN, Trinity College, Dublin, Ireland.

Small amplitude non-resonant AFM can determine both elastic and dissipative response of fluids in the narrow tip-surface gap. With sufficiently stiff levers, the system is stable at all separations, in particular during the oscillatory variations of stiffness with separation due to molecule size. The viscous term is shown to change from retardation to relaxation type behaviour at small separations. Using a lever sensitive also to lateral stiffness, both the viscosity and the shear modulus of fluid in very small gaps are found to depend strongly on the gap - molecule commensurability. The shear stiffness drops to very small values at incommensurate spacings. Possible consequences for modeling boundary layer flow are considered. Extrusion of thin

polymer films is critical for nano-imprint lithography. Results will be presented from nano-indentation, which shows the geometry and strain state, for the archetypal indent geometries of flat punch (for vias) and cavity (for mesas). It is shown that residual film thickness is limited not by polymer properties, but by elastic rigidity of the die, and that local nano-scale shear has a substantial effect on the larger scale deformation.

## 11:30 AM N1.7
### Measuring Interfacial Friction and Structural Detail with Combined Quartz Microbalance and Nanoindentation.

Brian Borovsky[1,2] and Adam Booth[2]; [1]Physics, St. Olaf College, Northfield, Minnesota; [2]Physics, Grinnell College, Grinnell, Iowa.

Even though new experimental methods have elucidated many fundamental aspects of friction in recent years, several key issues related to interfacial dynamics and structure remain poorly understood. Information on the response of molecularly thin lubricant layers to confinement and shear, and on the number and size of asperity contacts between randomly rough surfaces, is difficult to obtain due to the closed geometry of most interfaces. Furthermore, most of the widely used probe-based techniques do not access the high sliding speed regime relevant to technologies such as micromachined devices and hard disk drives. We therefore discuss a new technique that integrates a nanoindenter with a quartz crystal microbalance (QCM) to provide quantitative structural and dynamic information on microscale contacts subject to high frequency shear, reaching speeds over 1 m/s. We have studied the contact between a sapphire sphere and a polycrystalline gold electrode both with and without a self-assembled octadecanethiol monolayer film. We have extended previous work[1] by adding continuous monitoring of the QCM resonance bandwidth during indentations. We find that both the frequency and bandwidth of the QCM track changes in the contact area, as derived from the contact stiffness. Depending on the roughness of the gold electrode, variations in the frequency with contact area follow either the single-asperity or multi-asperity limits of the elastic no-slip model of the interface. These results reveal the number of individual contacts and clarify the extent to which a constant average size of asperity contacts is maintained independent of normal load.[2] However, the no-slip model fails to account for the large levels of dissipation observed during indentations, the dependence of the bandwidth on contact area, and the increase in both frequency and bandwidth shifts upon application of octadecanethiol films. We discuss refinements of the interaction model to account for both interfacial slip and the properties of polymer films under confinement. Research supported by NSF, Research Corporation, and Hysitron, Inc. [1]B. Borovsky, J. Krim, S.A. Syed Asif, and K. J. Wahl, J. Appl. Phys. 90, 6391 (2001). [2]J.A. Greenwood and J.J. Wu, Meccanica, 36, 617 (2001).

## 11:45 AM N1.8
### Dynamic response of the slip length at liquid/solid interfaces.

Nikolai V. Priezjev[1] and Sandra M. Troian[2]; [1]Mechanical Engineering, Michigan State University, East Lansing, Michigan; [2]Chemical Engineering, Princeton University, Princeton, New Jersey.

The existence and degree of slip at liquid-solid interfaces strongly influences transport behavior especially in micro- and nanofluidic devices where the surface to volume ratio can be exceedingly large. Slip is normally quantified through the slip length, defined as the distance within the solid phase where the extrapolated tangential flow speed vanishes identically. Here we consider the dependence of the slip length on the shear rate imposed within the liquid phase. Molecular dynamics simulations (MD) provide a powerful tool for extracting detailed correlations between the slip length and transport coefficients affecting the degree of molecular displacements near the wall. Such simulations have shown that the in-plane structure factor and diffusion coefficient, controlled by the wall-fluid interaction potential and liquid-solid density ratio, play especially significant roles in determining the degree of slip in equilibrium. Studies of sheared liquid films have uncovered a nonlinear relationship between the slip length and internal shear rate for both simple fluids and polymer melts. In this talk we focus on simple liquids subject to planar shear in a Couette geometry to uncover the molecular mechanisms leading to this nonlinear relationship. First, the results are recast in terms of the dependence of the frictional force at the interface on the average slip velocity at the solid wall. To gain insight into the mechanisms leading to this force law, we have performed statistical mechanical and MD studies of the collision events between the first liquid layer and the surface atoms comprising the solid wall. The most important contribution to the frictional force arises from the repulsive part of the Lennard-Jones interaction potential. These findings provide the molecular basis leading to the nonlinear dependence of the slip length on shear rate. Further support for this picture is obtained by consideration of two model systems: one involving a single fluid layer driven across the surface of an atomically flat wall composed of periodically arranged Lennard-Jones atoms and the other involving

the dynamics of a single molecule scattering from an atomistic wall. These models identify the source of the dynamic frictional response at low and intermediate shear rates as well as the saturation behavior at large sliding velocities. Time permitting, we will examine the statistics of single molecule collisions events in the context of slip in rarefied gas flows where Maxwells boundary condition replaces the Navier slip condition for liquid/solid interfaces.

## 1:30 PM *N2.1
### Boundary Lubrication Under Water.

Jacob Klein, [1]Oxford University, Oxford, United Kingdom; [2]Weizmann Institute, Rehovot, Israel.

Amphiphilic surfactant molecules, where a polar head group anchors a hydrophobic tail, have long been used to coat surfaces to reduce friction and wear between them as they rub past each other. Under water this behaviour may be strikingly different, not only in the magnitude of the frictional forces but also in the mechanism of lubrication. Several examples from different surfactants will be presented, and a common theme controlling their efficiency identified. * with Wuge Briscoe, Susan Perkin, Meng Chen, Uri Raviv, Bob Thomas

## 2:00 PM *N2.2
### Nano-Science Via Nano-Spectroscopy.

Steve Granick, Jeffrey Turner, Sung Chul Bae, Minsu Kim, Shan Jiang and Liang Hong; Materials Science and Engineering, Chemistry and Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois.

There is growing awareness that the interpretation of nanotriboloy and other careful force measurements at the molecular and atomistic levels will benefit from ancillary local probes such as those obtainable by in-situ spectroscopic and scattering measurements of the interface. This laboratory has devoted considerable effort to combining force measurements (between mica sheets in the surface forces apparatus) with real-time measurements using not only vibrational spectroscopy, especially Raman and surface-enhanced Raman, but also few-molecule fluorescence spectroscopy, especially fluorescence correlation spectroscopy and time-correlated single-photon counting. An integrated picture emerges in which prior interpetations based solely on force measurements require some aspects of major modification based on information from these ancillary local probes. Time permitting, it will also be demonstrated that tribological processing of molecularly-thin conjugated polymers can also be employed to achieve novel photoluminiscent properties.

## 3:30 PM *N2.3
### Probing the Nano-Hydrodynamics at Solid-Liquid Interfaces using Thermal Motion.

Lyderic Bocquet, Laurent Joly and Christophe Ybert; Laboratoire PMCN, Universite Lyon I, Villeurbanne, France.

Over the recent years, there has been a strong interest in the nano-hydrodynamics of liquids close to surfaces, in particular in the context of the developping fields of micro- and nano-fluidics. More specifically, the question of hydrodynamic slippage at solid walls has been extensively studied by different groups. Various experimental routes have been followed to address this question, based either on flow characterization close to surfaces using optical methods (such as FRAP in evanescent waves geometry, or microPIV velocimetry), or dissipation methods (such as pressure drop measurements, or Surface Force Apparatus -SFA- and Atomic Force Microscopy -AFM- measurements). While these various measurements do confirm an overall link between the hydrodynamic slippage and the wettability of the solid substrate, there is still a large debate about the magnitude of the slippage effect and possible flow-induced surface alteration (through generation/interaction with nanobubbles). In this work we have followed a completely different strategy to tackle this problem, allowing to probe the nanohydrodynamics at the solid-liquid interface without external forcing. We do not measure change of dissipation due to the boundary slippage, or change of flow patterns, thereby avoiding problems inherent to the presence of an external flow in all previous measurements. Rather we take advantage of the richness present in the natural fluctuations of the system to probe the dynamics close to the solid surfaces. The method is therefore similar in spirit to the passive microrheology technique, but here allowing to reach nanometer resolution for the dynamics at surfaces. The diffusion dynamics of colloidal tracers in water (latex or silica beads, 200nm in diameter) have been measured using FCS - Fluorescent Correlation Spectroscopy- in a confined geometry, with a varying width between

confining surfaces ranging between 200 nm to 4 microns. On hydrophilic surfaces (smooth plain pyrex) the width dependence of the diffusion coefficient is found to agree remarkably well with hydrodynamic predictions using no-slip boundary conditions at the walls. On the other hand, on hydrophobic surfaces (OTS coated) the diffusion coefficient deviates from the previous no-slip results. A prediction based on the existence of slippage at the wall yields a very good agreement with experimental data, leading to a slip length of b=18 nm on the hydrophobic surfaces. These results are in full agreement with recent SFA experiments by Cottin et al. and with previous numerical simulations. Globally it demonstrates that such technique is strongly sensitive to the local dynamics at the surface, allowing to nanometer resolution. The absence of any external forcing will make it a very valuable tool to understand and ultimately control giant (micrometric) slippage promoted by air pockets on hydrophobic surfaces.

**4:00 PM N2.4**
**Tribological Properties of Fatty Acids in Contacts of Different Adhesive Strength.** Marina Ruths[1,2], Sarah Lundgren[1,3], Katrin Boschkova[1] and Karin Persson[1]; [1]YKI, Institute for Surface Chemistry, Stockholm, Sweden; [2]Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts; [3]Department of Chemistry, Surface Chemistry, Royal Institute of Technology, Stockholm, Sweden.

We have studied the lubricating properties of fatty acids with varying degree of unsaturation adsorbed onto steel surfaces from hydrocarbon solvent. The adsorption behavior was studied using a quartz crystal microbalance (QCM). Comparisons of macroscopic friction and wear measurements with a pin-on-disc setup and measurements at the nanometer scale on a single-asperity contact, done with atomic force microscopy (AFM), allow an assessment of the friction-modifying properties of different types of structures in the confined films. The effects of adhesion, contact area and pressure on the friction force were investigated for adsorbed fatty acid monolayers immersed in ethanol or dried in $N_2$ gas. Associated amphiphile structures with favorable friction-modifying properties are formed at the surfaces already at very low solution concentrations, and a correlation is seen between the adsorption behavior of unsaturated fatty acids and their reduction of friction.

**4:15 PM *N2.5**
**Drops in Drops: Emulsions in Microfluidics.** David A. Weitz, Dept of Physics and DEAS, Harvard University, Cambridge, Massachusetts.

Microfluidic techniques allow precision control over minute amounts of fluids. This provides an ideal method for fabricating emulsion droplets. This talk presents a method for making single and multiple emulsions, and explores the new types of materials that can be produced from these methods. It will also present other potential uses of this technology.

**4:45 PM N2.6**
**Shear Banding in Dense Colloidal Crystals Under Oscillatory Force: Mechanisms for Phase Separation out of Thermodynamic Equilibrium.** Benny Davidovitch[1], Itai Cohen[1,2], Michael P. Brenner[1] and David A. Weitz[1,2]; [1]DEAS, Harvard University, Cambridge, Massachusetts; [2]Physics Dept., Harvard University, Cambridge, Massachusetts.

We use fast confocal microscopy to study the displacement of particles in a dense colloidal crystal under oscillatory shear. The colloids are neutral glass beads, whose diameter is $\sim$1 micron, immersed in a solvent and placed between parallel static and in-plane oscillating plates, $\sim$ 40 micron apart, where the amplitude and frequency of applied oscillations are controlled by a piezoelectric device. For high frequencies ($>$ 3Hz) or low strains ($<$0.1), the colloids admit a homogenous shear profile, whereas for low frequencies and high strains the flow profile splits into two bands, identified by small and high shear rates, respectively. Our set-up provides unprecedented advantages in exploring the fundamental mechanisms underlying non-inertial shear banding phenomena in complex fluids: (a) Direct imaging of the colloids displacement field at various applied frequencies and amplitudes shows no evidence of nonlinear behavior (such as sub/super harmonics). This observation enables us to conclude that shear banding in our system reflects an out-of-equilibrium coexistence between two linearly responding phases of the crystal: liquid-like and solid-like, respectively. In particular, we rule out the possibility that the observed shear banding reflects nonlinear rheology of dense colloidal crystals. (b) We show that the scales of our system make it an ideal tool to study the border between small size systems, to which microscopic theories must be applied, and large systems whose behavior follows continuum theories. In particular, we show that a measurable amount of slip exits near the plates, at all values of applied frequencies and amplitudes, and use

this data to extract rheological parameters of the crystal. Moreover, we show that even in the hydrodynamic limit, as the system size becomes infinite, slip effects form a singular perturbation that cannot be neglected, for any nonhomogenous flow of complex fluids under oscillatory shear. (c) The clear, reproducible shear banding profiles at wide range of applied frequencies and amplitudes enable us to study how the ratio between volumes of two coexisting phases is selected out of thermodynamic equilibrium. This feature makes our system a unique tool to quantitative testing of various possible mechanisms that can replace the role of chemical potential far from thermodynamic equilibrium.

SESSION N3
Chair: John T. Fourkas
Tuesday Morning, November 29, 2005
Room 202 (Hynes)

**8:30 AM *N3.1**
**Dynamic Force Spectroscopy on Specific Bonds.** Rudolf Merkel, Institute of Thin Films and Interfaces, Research Center Julich, Juelich, Germany.

Bioadhesion, i.e. cell-cell and cell-substrate adhesion, is mediated by specific bonds between surface molecules. In many physiological processes like cell locomotion or mechanical activity of tissues, these bonds are loaded by mechanical forces. One of the most fundamental questions in biomechanics is the one regarding the yield strength of bioadhesion. However, the interpretation of experiments on whole cells or even tissues is very difficult because here many different molecular bonds in widely varying local environments act simultaneously. Clear-cut conclusions on the mechanisms underlying mechanical toughness of bioadhesion can be best achieved in model systems by mechanical experiments on isolated specific bonds. In dynamic force spectroscopy single bonds are loaded with gradually increasing forces in the piconewton range which result in bond failure. The rate of force application is systematically varied and the resulting distributions of yield forces are recorded. Here we present one experimental approach to apply piconewton forces to single bonds and show results of experiments on model systems. We and other researchers in the field have observed that isolated bonds between biomolecules fail under load in a stochastic way. The rate of bond failure is strongly influenced by tiny forces of some piconewtons acting on the bond. This surprising behavior can be explained by basic principles from reaction rate theory. Two fundamental parameters can be extracted from the data, namely a reaction rate, $k_o$, in the absence of force and the distance between bound state and activation energy barrier dominating bond dissociation. Surprisingly, the reaction rate in absence of force, $k_o$, is strongly influenced by the fact that the molecules are bonded to surfaces of the force measuring device. This gives rise to a substantial reduction in bond life time which depends on the stiffness of the force measuring device. A similar reduction in bond life time should also occur in bioadhesion where specific bonds connect soft surfaces as well. Finally, we show that the most important result of these experiments, time dependent mechanical strength of bioadhesion, holds as well in the physiologically important case of many bonds sharing the mechanical load.

**9:00 AM *N3.2**
**Looking into the dynamics of single molecules.** Joseph Klafter, Chemistry, Tel Aviv University, Tel Aviv, Israel.

Recent work on the fluctuations and catalytic activity of single enzymes will be summarized, emphasizing the highly nonexponential distribution in the enzyme activity and time autocorrelation. Ways to model this dynamical behaviour will be discussed.

**9:30 AM N3.3**
**Low Temperature Single Molecule Spectroscopy of MEH-PPV Conjugated Polymer Molecules.** Doo Young Kim, Young Jong Lee, John K. Grey and Paul F. Barbara; Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas.

Single molecule spectroscopy of the conjugated polymer MEH-PPV is investigated at cryogenic temperatures. The low temperature microsecond dynamics of single MEH-PPV conjugated polymer molecules are compared to the dynamics at room temperature revealing no detectible temperature dependence. The lack of temperature dependence is consistent with the previous assignment of the dynamics to a mechanism that involves intersystem crossing and triplet-triplet annihilation. Also, the fluorescence spectra of single MEH-PPV molecules at low temperature are studied as a function of excitation wavelength (i.e. 488, 543, and 568 nm). These results exhibit nearly identical fluorescence spectra for different excitation wavelengths. This strongly suggests that electronic energy transfer occurs efficiently to a small number of low energy sites in the

multichromophoric MEH−PPV chains.

**10:15 AM *N3.4**
**Translocation and unzipping kinetics of DNA molecules using a nanopore.** <u>Amit Meller</u> and Jerome Mathe; Rowland Institute at Harvard, Harvard University, Cambridge, Massachusetts.

Negatively charged biopolymers such as DNA and RNA can be electrophoretically driven through a single ∼1.5 nm alpha Hemolysin pore embedded in a phospholipid bilayer. By measuring the ion current flowing through the pore when the biopolymer is threaded, we can detect the passage time (translocation) of each DNA molecule. We found that the translocation dynamics is dominated by the DNA-pore interactions that depend strongly on the DNA sequence as well as on its direction of entry inside the pore, even for homopolymers such as Poly(dA)1. We also use our nanopore to unzip structured DNA and RNA molecules at the entry to the pore, and study their unzipping kinetics2. Our method allows us to apply force directly on the test molecule eliminating the need for molecular linkers. In this talk I will discuss our experiments, and present results from molecular dynamics simulations of DNA translocation. 1. Mathe J., Aksimentiev A., Nelson D., Schulten K. and Meller A. Proc. Natl. Acad Sci., in press. 2. Mathe J., Visram H., Viasnoff V., Rabin Y. and Meller A. Biophys. J., 87, 3205 (2004).

**10:45 AM N3.5**
**Lateral Mobility in Membranes Revisited: A Simpler Law from Peptides to Large Proteins?** <u>Yann Gambin</u>, Ricardo Lopez, Myriam Reffay and Wladimir Urbach; LPS de l'ENS, Paris, France.

The study of lateral mobility is widely used to obtain valuable information about membrane proteins incorporated into cells, vesicles or supported bilayers. To answer the questions whether a protein is monomeric or multimeric, whether a peptide is lying on a membrane or spanning the bilayer, diffusion measurements can be considered as fast and fruitful. If for lipid-size molecules, a "jumping" movement due to local defects of packing in the bilayer is accepted, peptides and transmembrane proteins are in contrast supposed to translate in a perfectly continuous medium, ignoring the finiteness of the lipids. The model of Saffman-Dellbruck predicts the diffusion coefficient D of a simple cylinder embedded in a thin sheet of fluid that matches its height. In its formula, the variables are by order of importance: the thickness h and viscosity $\mu$(m) of the membrane, the radius of the protein R and the viscous coupling to the aqueous phase through its viscosity $\mu$(w). D= (kT/4$\pi\mu$(w)h)*(ln($\mu$(m)h/$\mu$(w)R)-0.5772) Despite the fact that most of biological studies refer to that model to characterize radii of proteins, the model was never thoroughly investigated. In order to weight the importance of each parameter of the above relation we selected Pattern Photobleaching under microscope to measure precisely the self-diffusion of well-known transmembrane peptides and proteins in various bilayers. We tested : - the role played by the hydrophobic thickness h of the membrane, we designed a versatile phase of model bilayers made of "soft", non-ionic surfactants (C12E5). These bilayers are indeed swollen at will, as a hydrophobic solvent spontaneously inserts between the monolayers and increase continuously h from 16 to 40 A. - the role played by the radius R of teh diffusing objetc. We incorporated three large proteins OmpA, OprM and Bacteriorhodopsine (R=11, 15 and 18 A). The D variation with R is dramatically larger than anticipated by Saffman's model. Our, as well as literature, experimental results indicate that the diffusion coefficients is rather inversely proportionnal to the radius R of diffusing object. One can write D= kT.a / (4$\pi\mu$(w)hR) where "a" would be a pertinent length, characteristic of the membrane, over which the velocity variation occurs in the bilayer. This simple, heuristic law allows us furthermore to quantify the size of the perturbation created by several transmembrane peptides, longer or shorter than the membrane itself, and leads to results in good agreement with IR Spectroscopy and MD simulations.

**11:00 AM *N3.6**
**Coupled Dynamics of DNA-Breathing and Selectively Single-Stranded DNA-Binding Proteins.** <u>Ralf Metzler</u>, Tobias Ambjornsson and Suman K. Banik; Nordita, Copenhagen OE, Denmark.

The talk will start with an introduction to DNA and its physical properties. Although the double-helical DNA structure is thermodynamically stable, locally it can come apart easily due to thermal fluctuations, producing intermittent single-stranded nanosize DNA bubbles of finite lifetime. I will introduce a dynamical model for this DNA-breathing on the basis of a discrete master equation for both homo- and heteropolymer sequences. It turns out that the bubble-dynamics is sensitive to the DNA-sequence. Apart from this probabilistic approach, I will also show the results of a stochastic Gillespie reaction scheme producing a single-bubble time series. In the second part of the talk, I will address the long-standing puzzle why the presence of selectively single-stranded DNA-binding proteins

(SSBs) does not lead to full denaturation of the DNA, although it would correspond to the thermodynamically favourable state. Inspired by recent single molecule experiments, I will discuss the effects of the presence of SSBs to the dynamics and thermodynamics of the DNA-bubbles. Under certain conditions, SSBs can induce full denaturation of DNA.

**11:30 AM N3.7**
**An Improved Way to Analyse Proteins Interactions.** <u>Myriam Reffay</u>[1], Houssein Benabdelhak[2], Yann Gambin[1], Arnaud Ducruix[2] and Wladimir Urbach[1]; [1]Laboratoire de Physique Statistique, PARIS, France; [2]Laboratoire de R.M.N. et Cristallographie Biologiques, PARIS, France.

Pseudomonas Aeruginosa is a Gram-negative bacteria i.e. a bacteria with a double membrane. It develops a multidrug resistance to antibiotics. Such a resistance owes much to efflux pumps which are responsible for taking toxins out of the cell. Efflux pumps are composed of three proteins. The most important identified association is constituted of the three proteins named MexA, MexB and OprM. Indeed the pump consists of the inner membrane-spanning proton-antibiotics antiporter protein MexB, the outer membrane associated protein OprM and the membrane fusion protein MexA assumed to connect the inner and outer membranes. Our aim is to understand the way the proteins interact to find the function of each of them and to test pump inhibitors in order to increase antibiotics action on bacteria. First, we decided to focus on the periplasmic protein MexA to elucidate its function. We study its interaction with the outer membrane protein OprM to find out whether MexA is involved in the recruitment of the outer membrane protein. To analyse binding reactions we have selected the study of the lateral mobility by photobleaching methods. Diffusion measurements are widely used to obtain information about the property of membrane proteins such as their radius, their multimerization degree, or to test their anchoring to membranes. These experiments seem to be one of the best ways to test interactions. What are the advantages of such a process compared to well-known experiments such as Biacore? First of all, proteins are incorporated in model bilayers representing a biomimetic membrane or a double membrane in our case. Furthermore this system allows us to modify the bilayer thickness and the water size between them. We can thus test the size and the orientation of the interaction, answering the questions: which parts of the proteins interact and how they bind together. With this experiment, we manage to measure unbiding times between two components of the pump MexA and OprM and to access to interaction energy of the two associated proteins. In conclusion fluorescence techniques provide a useful and fruithful way to test and to study interactions between proteins.

**11:45 AM N3.8**
**Transport of DNA through carbon nanotube in an aqueous environment: A molecular dynamics study.** <u>Maodu Chen</u> and Yongqiang Xue; College of Nanoscale Science and Engineering, University at Albany-SUNY, Albany, New York.

Molecular dynamics simulations have been carried out to study the transport process of single-stranded and double-stranded DNA through single-walled carbon nanotube and the nanochannel constructed with carbon nanotube array in an aqueous environment. The Amber force field is used to describe the interaction of atoms in the system and the Amber molecular dynamics package is employed to perform the molecular dynamics simulations. A rapid inserting process of DNA inside into the carbon nanotube and the nanochannel has been observed. The dependence of transport dynamics on the type of the carbon nanobute, the size of the nanotube, the sequence of the DNA, and the salt concentration etc has been investigated. The simulations can provide valuable insights into the transport of DNA through nanoscale pore or channel structures which occur in many biological processes.

SESSION N4
Chair: Pierre Levitz
Tuesday Afternoon, November 29, 2005
Room 202 (Hynes)

**1:30 PM *N4.1**
**Cell locomotion and cellular oscillations.** <u>Frank Julicher</u>, Max Planck Institute for the Physics of Complex Systems, Dresden, Germany.

Living cells are highly dynamic. This dynamics results from active processes on the molecular scale. On the cellular scale, complex dynamic phenomena emerge, such as cell locomotion on a substrate or cell division. I will present simplified descriptions of cellular dynamics in two examaples. During cell locomotion, the cytoskeleton, which is a gel of actin filaments, is constantly remodeled. At the leading edge,

new gel is polymerized, in the rear the gel is disassembled. The gel itself has active properties because of the action of motor proteins which leads to contractile properties of this effective material. I will outline a hydrodynamic theory of this active polar gel and discuss how general features of cell locomotion can be captured by such a description. A second example concerns oscillations which occur during the division of some cells. A more specific description of the interplay of motor proteins with filaments of the mitotic spindle aparatus naturally leads to oscillations if the number of motors is increased. The observation of oscillations of the spindle thus provides a signature of underlying dynamics and force generation during cell division.

**2:00 PM *N4.2**
**Phase Diagram of Nucleosome Core Particles.**
Francoise Livolant[1], Stephanie Mangenot[1], Amelie Leforestier[1] and Dominique Durand[2]; [1]Laboratoire de Physique des Solides, CNRS -UMR8502, Orsay, France; [2]IBBMC, CNRS, Orsay, France.

The nucleosome core particle consists of a protein octamer, with two copies of the four histones (H2A, H2B, H3, H4) and 146bp of DNA wrapped around in a left-handed helix [1]. DNA overcharges the protein core and the resulting net charge is about 150 e-. This complex forms a flat rigid cylinder, 110A in diameter and 57A high from which the flexible and basic terminal histone parts, usually called the tails, may extend. In the living cell, these particles, connected to each other by linker DNA fragments, are concentrated up to 100-500 mg/ml but their supramolecular ordering remains unknown. A few years ago, we began a systematic analysis of the phases formed by the isolated NCPs under concentrations that are biologically relevant. These dense phases can be prepared experimentally in two different ways : i) in the presence of monovalent salt (3.5 to 160mM NaCl) under controlled osmotic stress [2] or ii) by addition of multivalent cations (Mg2 , spermidine3 , spermine4 ) that induce the aggregation of NCP [3-4]. Although this experimental system is extremely simplified and does not reproduce all details of chromatin in the living cell, these phases constitute a library of structures that may possibly exist in vivo since they were found under biologically relevant salt and NCP concentration ranges. We present here the phase diagram of these NCP under a large range of monovalent ion and NCP concentrations. A remarkable self-assembly property of NCP is to form columns, by stacking on top of each other. For higher pressures (concentrations), these columns further align to form either columnar hexagonal phases (2D or 3D) or a lamello-columnar phase followed by an inverse hexagonal phase. Slight changes of the ionic conditions are enough to induce rapid phase transitions, significant change in the NCP concentration and DNA accessibility. We will focus on the phases observed under low monovalent salt condisions [5], and show how the chiral and electrostatic properties of the NCP combine to form original tubular and spherulitic structures. References [1] K. Luger, et al., Nature 389 (1997) 251. [2] S. Mangenot et al., J. Mol. Biol. 333 (2004) 907. [3] M. de Frutos et al., Biophys. J. 81 (2001) 1127. [4] A. Leforestier et al., J. Mol. Biol. 290 (1999) 48. [5] A. Leforestier et al., Biophys. J. 81 (2001) 2414.

**3:30 PM *N4.3**
**Magnetophotonic and Electrophotonic Nano-Devices for Imaging Chemical and Physical Dynamics in Micro-Environments and Inside Live Cells.** Raoul Kopelman, Jeffrey Anker, Caleb Behrend, Brandon McNaughton and Katherine Tyner; Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

Hybrid nano-tools, combining photonic, mechanic, magnetic, electric and chemical components, open the way for measuring and imaging dynamic properties in complex microdomains or microenvironments, such as inside biological cells. A combination of "bottom up" and "top down" techniques are used for optimal fabrication of these structured nanoparticles. These miniature systems integrate magnetic, photonic, chemical and biological functions and activities. Examples are: 1) micro/nano-sensors inside live cells for real-time, spatially resolved chemical imaging; 2) nano-sensors inside live cells for real-time, spatially resolved imaging of the dynamics and dynamical moduli of the sub-cellular nano-environment. Magnetic modulation of the sensors dramatically enhances the fluorescence signal/background ratio. Magnetic modulation exhibits non-uniform oscillator behavior, which enables measurements of local viscosity or micro-rheology. Non-magnetic "Brownian MOONs," consisting of half-shell reflective, half-shell transmissive nanoparticles are also used for optical modulation and as nano-viscometers. Photonic nanosphere electric field sensors have been produced and tested. These smallest "voltmeters" are made for both high and low field measurements in biological or other micro-environments.

**4:00 PM *N4.4**
**Isomerization Dynamics of Photochromic Spiropyran Molecular Switches in Phospholipid Bilayers.** Darius Kuciauskas

and Christopher J. Wohl; Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia.

Phospholipid bilayer aggregates, such as liposomes, are used as cell membrane models. Restrictive environment and specific molecular interactions in phospholipid bilayers affect chemical reactions in these systems. Studies of reactions in phospholipid bilayers enable determination (or modification) of membrane properties. In this work, we investigated ultrafast ring opening and isomerization reactions of photochromic spiropyran compounds in phosphatidylcholine (DMPC, DPPC, and DOPC) bilayers. After excitation with UV photons, colorless spiropyran (SP) compounds are converted to colored merocyanine (MC) products on the picosecond time scale. The MC product is not formed directly from the spiropyran S1 state, but from the intermediate state, X. Competition between the internal conversion and isomerization determines MC yield. Isomerization dynamics in phospholipid bilayers differs from those in organic solvents; these effects were attributed to the viscosity variations and free volume changes in the phospholipid bilayer gel ($P_\beta$) and liquid ($L_\alpha$) phases. Activation energies for the isomerization reaction in DMPC bilayers were Eiso =26.0±1.0 kJ/mol in liquid $L_\alpha$ phase and Eiso =7.3±1.6 kJ/mol in gel $P_\beta$ phase. Following ring opening and isomerization in the aliphatic region of the phospholipid bilayer, MC diffuses to the lipid headgroup region. Linear dichroism and solvatochromism measurements were used to determine MC localization. It was found that MC dipole moment distribution function has a maximum at ∼15° angle to the bilayer normal.

**4:30 PM N4.5**
**Dispersion in Active Transport by Kinesin-Powered Molecular Shuttles.** Takahiro Nitta[3,2] and Henry Hess[3,1];
[1]Materials Science and Engineering, University of Florida, Gainesville, Florida; [2]Department of Mathematical and Design Engineering, Gifu University, Gifu, Japan; [3]Dep. of Bioengineering, University of Washington, Seattle, Washington.

Active transport driven by molecular motors is a key technology for the continued miniaturization of lab-on-a-chip devices, because it is expected to enable nanofluidic devices with channel diameters of less than 1 micrometer and total channel lengths on the order of 1 mm. An important metric for a transport mechanism employed in an analytic device is the dispersion, because it critically affects the sensitivity and resolution. Here, we present an investigation into the mechanisms responsible for the dispersion of a swarm of molecular shuttles, consisting of functionalized microtubules propelled by surface-adhered kinesin motor proteins. Using a simple model and measurements of the path persistence length, motional diffusion coefficient and the distribution of average velocities we found that, at the time scale relevant in the envisioned nanobiodevices, variations in the time-averaged velocities between shuttles will make a stronger contribution to the dispersion of the swarm than fluctuations around the time-averaged velocity of an individual shuttle or the fluctuations in path length due to wiggling within the channel. Overall, the dispersion of such molecular shuttles is comparable to the dispersion of a sample plug transported by electroosmotic flow. From a fundamental point of view, our measurements yielded three interesting findings: (1) The persistence length of the microtubule trajectory is an order of magnitude smaller than the persistence length of the microtubule itself, against expectations [1]. (2) The motional diffusion coefficient of the microtubule gliding on many motors is similar to the motional diffusion coefficient of an individual motor walking along a microtubule [2], suggesting cooperativity between motors. (3) Velocities of gliding microtubules deviate by a few percent between microtubules. A related publication is in print in Nano Letters. 1. Duke, T.; Holy, T.E.; Leibler, S. Phys. Rev. Lett. 1995, 74, 330-333. 2. Svoboda, K.; Mitra, P.P., Block, S.M. Proc. Natl. Acad. Sci. U S A, 1994, 91, 11782-6.

**4:45 PM N4.6**
**Novel Nanoscale Electromechanical Phenomena in Biological and Inorganic Systems.** Sergei V. Kalinin[1], Vincent Meunier[2], Stephen Jesse[1], Alexi Gruverman[3], Brian J. Rodrigues[1,3], W. L. Liu[4] and A. A. Balandin[4]; [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [3]Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; [4]Nano-Device Laboratory, Department of Electrical Engineering, University of California - Riverside, Riverside, California.

Electromechanical coupling is a universal feature of polar materials, originating at molecular levels and directly related to bond dipole moments. In crystalline materials, the spectrum of possible electromechanical phenomena is limited by the bulk symmetry. Novel electromechanical phenomena such as surface piezoelectricity and surface and quantum flexoelectricity arise on the nanoscale but are either forbidden or undetectable for bulk materials. Until recently, the

necessity of measuring femtoamp currents or picometer displacements precluded direct probing and interpretation of these phenomena. We demonstrate scanning probe microscopy for local imaging and spectroscopy of nano-electromechanical phenomena. For molecular materials, we show that the electromechanical signal is directly related to local molecular orientation and the degree of ordering. Experimental measurement of molecular orientation is demonstrated for several inorganic and biological systems. For many biological materials, the complex hierarchical structure results in an indirect relationship between electromechanical coupling on molecular and fibril levels and macroscopic properties. We image the piezoelectric textures of materials such as dentin that do not posses piezoelectric coupling on a macroscopic scale and demonstrate that these materials are mesoscopically antipiezoelectric due to averaging between antiparallel piezoelectric domains. Finally, the electromechanical imaging of tobacco mosaic virus is illustrated. In this case, the cylindrical symmetry of the structure forbids macroscopic piezoelectric coupling. Possible contributions of inhomogeneous tip field and surface flexoelectricity to PFM contrast are discussed. Approaches for the interpretation of electromechanical contrast based on density functional theory modeling and future opportunities of electromechanical SPM for characterization of complex systems are presented.

SESSION N5
Chair: Joseph Klafter
Wednesday Morning, November 30, 2005
Room 202 (Hynes)

**8:30 AM *N5.1**
**Water Mobility in Reverse Micelles from Quasielastic Neutron Scattering and Molecular Dynamics Simulation.**
Branka Maria Ladanyi[1], Michael R. Harpham[1], Nancy E. Levinger[1] and Kenneth W. Herwig[2]; [1]Department of Chemistry, Colorado State University, Fort Collins, Colorado; [2]Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Reverse micelles (RMs) are aggregates in which nanoscale droplets of a polar liquid, usually water are surrounded by a surfactant layer in a nonpolar continuous phase. They are widely used as media for reactions in which the extent of confinement or the presence of a surfactant interface play a central role. We have used molecular dynamics (MD) computer simulation and quasielastic neutron scattering (QENS) and to investigate the mobility of water molecules in reverse micelles. The contribution of water to the QENS signal is enhanced by deuterating the surfactant and the nonpolar phase. Our studies of water mobility have focused on the effects of water pool size, determined by water/surfactant mole ratios w0, as well as on the properties of the water-surfactant interface. Specifically, we have examined the effects of counterion size and charge in the case of the anionic AOT (bis (2-ethylhexyl) sulfosuccinate)) surfactant and the role of the alcohol cosurfactant in the case of the cationic surfactant cetyl ammonium bromide (CTAB). We find good agreement between the QENS signal and its prediction from MD simulation of the self-intermediate scattering function (ISF) of water hydrogens. This allows us to obtain additional insight into water mobility by analyzing the ISF in terms of the effects of confinement and of contributions from molecular rotation and translation and from molecules in different interfacial layers.

**9:00 AM *N5.2**
**Nanoscopic Water Dynamics Probed with Ultrafast Infrared Vibrational Echo and Pump-Probe Experiments.**
Michael D. Fayer, Ivan R. Piletic, David Moilanen and David Ben Spry; Chemistry, Stanford University, Stanford, California.

In many processes, water does not exist in its bulk form, but rather in nanoscopically confined environments. Nanoscopic pools of water are important in biology, geology, materials processing, and chemistry. The dynamics of nanoscopic pools of water (4.0 to 1.7 nm diameter, ~1000 to ~50 water molecules) in AOT reverse micelles are directly investigated for the first time using frequency selective infrared vibrational echo experiments on the water, and the data are compared to bulk water data. The nanopool data are substantially different from the bulk water data and show a clear size dependence. The data are analyzed theoretically to determine the frequency-frequency correlation function. The fastest dynamics (~50 fs) are similar to bulk water, but the slowest dynamics, i.e., global hydrogen bond network structural rearrangements (making and breaking of hydrogen bonds), are ~10 times slower, and slow substantially as the nanopool size is reduced. Ultrafast infrared pump-probe experiments are also used to address the dynamics of water in reverse micelles by measuring the orientational relaxation times of the water molecules. Reverse micelles with water nanopool diameters ranging from 1.7 nm to 28 nm are studied. The smaller water nanopools display highly non-exponential

decays, while the larger ones are single exponentials. The data are analyzed in terms of an ultrafast inertial component followed by restricted orientational relaxation (wobbling-in-a-cone) and final orientational diffusion to complete orientation randomization. The results demonstrate that bulk water characteristics are not obtained until the water nanopools approach 30 nm in diameter. The results are compared to molecular dynamics simulations.

**9:30 AM N5.3**
**Ultrafast Orientational Dynamics of Nanoconfined Benzene.**
John T. Fourkas[1,2], Xiang Zhu[1,2] and Richard A. Farrer[2]; [1]Chemistry and Biochemistry, University of Maryland, College Park, Maryland; [2]Chemistry, Boston College, Chestnut Hill, Massachusetts.

Ultrafast optical Kerr effect spectroscopy has been used to study the orientational dynamics of benzene and benzene-d6 confined in nanoporous glasses with a range of different average pore diameters. Both liquids exhibit biphasic OKE decays, with one decay component corresponding to bulk-like molecules in the pore centers and the other arising from a monolayer of molecules interacting with the pore surfaces. There are significant differences between the surface dynamics of the two liquids that presumably arise from differences in surface energies. Comparison to Raman data indicates that there is a high degree of ordering of molecules at the pore surfaces. Modification of the pore surfaces with trimethylsilyl groups leads to faster surface orientational dynamics and a thinning of the surface layer that is interpreted in terms of the orientations of molecules at the modified surfaces.

**10:15 AM *N5.4**
**Vibrational Energy Transfer in Reverse Micelles.**
Yoonsoo Pang[1], John C. Deak[2], Timothy D. Sechler[2], Zhaohui Wang[1] and Dana D. Dlott[1]; [1]School of Chemical Sciences, University of Illinois, Urbana, Illinois; [2]Department of Chemistry, University of Scranton, Scranton, Pennsylvania.

Ultrafast nonlinear vibrational spectroscopy is used to study vibrational energy transfer in reverse micelles. The technique used combines a subpicosecond IR excitation pulse with incoherent anti-Stokes and Stokes Raman probing. The Raman probe technique lets us probe vibrational excitations in all the system vibrations simultaneously. With this method it is possible to follow, in real time, the flow of excitation within the water nanodroplet and within the surfactant monolayer. It is also possible to watch vibrational energy flow from the water across the surfacant monolayer into the nonpolar surroundings. Vibrational energy flow across a surfactant can behave quite differently from ordinary heat flow, and the precise pathways depend on the details of the molecular structures. Reference: Deak J. C., Pang Y., Sechler T. D., Wang Z., Dlott D. D. 2004. Vibrational energy transfer across a reverse micelle surfactant layer. Science 306: 473-476.

**10:45 AM N5.5**
**Small Molecule Diffusion in Polymer Ultra-Thin Films.**
Ivan Ordaz, Peter J. Ludovice and Clifford L. Henderson; School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The diffusion of small molecules is critically important in a variety of applications ranging from membrane based separations to microelectronics fabriation. We have recently published results showing drastically reduced diffusion coefficients for small molecules in polymer ultra-thin films ranging in thickness from 30 nm to 400 nm. These diffusion coefficient reductions occur in films at significantly larger film thickness length scales than those reported for other polymer confinement phenomena such as polymer glass transition temperature deviations. Our recent work has focused on probing the effect of polymer molecular weight and thermal history on the film diffusion behavior. This work has shown that the film thickness at which diffusion coefficients are observed to change, relative to bulk film properties, scales with the polymer molecular weight. Furthermore, we have pursued the use of both molecular simulation and positron annhilation lifetime spectroscopy (PALS) to probe the free volume content and disribution in such polymer ultra-thin films. It does appear that changes in the polymer free volume distribution occur at small film thicknesses and these free volume changes can at least partially explain the observed results. This paper will present an update on our experimental and simulation work on the diffusion behavior of small molecules in polymer ultra-thin films and will discuss the impact of this behavior on several applications areas.

**11:00 AM *N5.6**
**A Bimodal Density of States for Conjugated Polymers.**
Paul F. Barbara, Doo Young Kim and John K. Grey; Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas.

The near-band-edge energy region of the density of electronic states

(DOS) of the conjugated polymer MEH-PPV has been investigated by low temperature fluorescence single molecule spectroscopy (SMS). An extensive set of high signal-to-noise SMS data have been acquired for MEH-PPV samples as a function of molecular weight confirming the previously reported *bimodal energy gap distribution*. A molecule by molecule vibronic analysis has yielded an experimentally determined spectral density of the $S_0$-$S_1$ energy gaps for the individual chromphores for MEH-PPV. The SMS data has also led to new insights on the energy transfer pathways for conjugated polymers, and on the molecular nature of the "blue" and "red" sites of conjugated polymers. Finally, a combined analysis of the new SMS data with the previously obtained bulk absorption and emission data for MEH-PPV has offered clear evidence that the near-band-edge energy region DOS for MEH-PPV, in analogy to the emission spectral density, exhibits a bimodal energy gap distribution.

**11:30 AM N5.7**
**Nanocharacterization of Relaxation Properties in Organic Thin Film Electronic Materials.** Rene M. Overney and Tomoko Gray; Chemical Engineering, University of Washington, Seattle, Washington.

In general, the pursuit for highly efficient electronic organic materials is limited by the molecular mobility and its control. For instance, to achieve a large electro-optical activity in non-linear dipole chromophore systems, one needs to control their susceptibility to undesired aggregation during the forced aligning process (poling) of the chromophores. With the growing complexity of the molecular building blocks of electronic organic materials, and the decreasing system sizes (e.g., ultrathin films) the characterization tools have to evolve. In this paper, we present a nano-rheological technique based on scanning force microscopy that offers a quantitative approach for investigating the mobility/stability of organic semiconductors ultrathin films. Local properties such as energy barriers for sub-molecular motions (relaxations) and critical transition temperatures can be measured directly on films on relevant substrates (e.g., ITO glass) that are later used in actual devices. Recent results related to photonics and optoelectronics are discussed, such as the improvement of the optical efficiency and the enhancement of the spectral stability.

**11:45 AM N5.8**
**Abstract Withdrawn**

SESSION N6
Chair: Raoul Kopelman
Wednesday Afternoon, November 30, 2005
Room 202 (Hynes)

**1:30 PM *N6.1**
**Charge Control in Electrowetting-Induced Microdroplet Generation.** Frieder Mugele, Physics of Complex Fluids, University of Twente, Enschede.

Electric fields are a versatile tool both for the manipulation and for the generation of liquid droplets in microfluidic applications. Here, we present an experiment that combines both aspects. Liquid droplets in a standard electrowetting configuration are induced to oscillate periodically between two morphologies, one in which the droplet is attached to a wire that is barely immersed into the droplet at zero voltage, and a second one in which the droplet is detached from the wire. As the droplet oscillates between the two morphologies, it forms a thin capillary neck that eventually pinches off in each oscillation cycle. The charge of the droplet immediately after the detachment is determined is determined by the relation between the frequency of the applied AC voltage and the RC time constant of the droplet which diverges as the diameter of the capillary neck vanishes. For high frequency (or low liquid conductivity) the droplet is discharged during the pinch off process resulting in an abrupt increase of the contact angle. Under these conditions, the droplet oscillation dynamics are entirely determined by the hydrodynamic response of the system to the abrupt contact angle variation upon breaking or re-establishing the connection to the wire. This is evidenced by the good agreement between the experimental surface profiles and corresponding computational fluid dynamics calculations using the volume of fluid method. As an application we demonstrate that self-excited droplet oscillations can be used to promote mixing in digital microfluidic devices. Finally, we emphasize that the discharging mechanism presented here is applicable to any situations involving electric field-induced droplet generation, such as continuous inkjet printing or electrospray ionization.

**2:00 PM *N6.2**
**Phase Transitions and Criticality in Confined Systems.**
Alexander V. Neimark, TRI/Princeton, Princeton, New Jersey.

Phase transformations in small confined systems, which demonstrate characteristic signatures of 1st order phase transitions, have been extensively documented in experiments and molecular simulations of various systems ranging from molecular clusters to thin films to pore fluids. From the positions of statistical mechanics, a rigorous interpretation of these observations represents a fundamental problem. We deal with essentially small, finite volume systems, in which the thermodynamic functions are analytical so that the very definition of phase transitions has to be revisited. The concept of the thermodynamic limit is no longer valid, and the statistical ensembles (canonical and grand canonical) are not equivalent. The phase transitions in finite systems are characterized by a convexity anomaly of thermodynamic potentials and van der Waals-type caloric curves and isotherms. We present a rigorous statistical mechanical framework for the description and molecular simulations of phase transitions in small confined systems, which is based on the mesoscopic canonical ensemble (MCE) [1]. The sample system is considered in chemical equilibrium with a finite reservoir of ideal particles called the gauge cell. By varying the gauge cell volume, one can control the level of density fluctuations in the sample system and study the states that are stable in the canonical ensemble yet unstable (or metastable) in the grand canonical ensemble. The method is illustrated on the example of vapor-liquid transition (capillary condensation) in spherical cavities. [1].A.V. Neimark and A. Vishnyakov, JCP, 2005, in press.

**3:30 PM *N6.3**
**Optical Study of Helium Adsorption and Desorption in Silica Aerogels.** Thierry Lambert[1], Florence Despetis[2], Laurent Puech[1] and Pierre-Etienne Wolf[1]; [1]Centre de Recherches sur les Tres Basses Temperatures, Centre National de la Recherche Scientifique, Grenoble, France; [2]Laboratoire des Colloides, Verres, et Nanomateriaux, Centre National de la Recherche Scientifique, Montpellier, France.

We present a study of the condensation of helium 4 into silica aerogels, addressing questions still debated in the field of porous media: What is the origin of the hysteretic behavior of the amount adsorbed as a function of pressure? Is capillary condensation a relevant concept for a gel of strands? Or are adsorption and desorption better described by recent theories, according to which disorder and interconnectivity are key elements (F. Detcheverry et al, Langmuir 20, 8006 (2004))? Using helium is advantageous because of its low surface tension, which minimizes the deformation of the gel upon adsorption. Furthermore, its optical index is close to unity, resulting in single scattering even for strong spatial density fluctuations. We have used spatially resolved light scattering in combination with pressure measurements along isotherms to study the condensation of helium between 4.4 K and Tc=5.2 K. In order to assess the influence of microstructure, we have used two aerogel samples synthesized in Montpellier with the same 95% porosity, but different microstructures depending on the pH of synthesis (basic or neutral). As in other porous media, we find hysteresis between adsorption and desorption close to the saturated vapor pressure. The position (in pressure) of the loop is consistent with a mechanism of capillary condensation into effective pores whose radius is of order the coherence length of the gel (several tens of nanometers). Such a mechanism also accounts for the smoother shape of the loop for the neutrally catalyzed sample, as the distribution of 'pores' sizes is wider in this case. This mechanism does not explain the observed change in the loop shape, as a function of temperature, for the base-catalyzed sample. Smooth below the critical point, the loop becomes sharp (i.e. adsorption and desorption take place at well defined pressures) when the temperature is low enough. In contrast, this change is in qualitative agreement with the Detcheverry et al. predictions. In parallel to the isotherms, the optical signal allows to detect the initial growth of a film onto the silica, followed by the growth of 'droplets' along the adsorption branch of the hysteresis loop. The droplets size reaches several hundreds of nanometers (about ten times the gel correlation length) at complete filling. Remarkably, whereas this growth is homogeneous over the whole sample when the loop shape is smooth, the droplets macroscopic distribution is heterogeneous when the loop is sharp. The Detcheverry et al. mechanism could provide a natural explanation of this behavior in terms of an enhanced sensitivity to the silica heterogeneities. Finally, for a given adsorbed amount, the optical signal is nearly identical between adsorption and desorption for the neutrally catalyzed sample. This symmetry between condensation and desorption events is at odds with the scenario of pore-blocking, but also with the predictions of the Detcheverry et al. approach.

**4:00 PM N6.4**
**Numerical Simulations of Change of Criticality for Systems Confined in Aerogels Pores.** Remi Jullien[1], Carlos Vasquez[2], Ricardo Paredes[2] and Anwar Hasmy[2]; [1]LCVN, Universite Montpellier 2, Montpellier, France; [2]IVIC, Universidad Simon Bolivar, Caracas, Venezuela.

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We review recent results on the effect of a certain type of correlated disorder on two well-known O(n)-vector models in three dimensions, namely the Ising and 3DXY models. Experimental evidences of changes in criticality of both systems, when confined in aerogel pores, are briefly referenced. The latter is known to represent the universality class to which bulk superfluid 4He at its lambda transition belongs. Experimental realizations of the former have been made in the past through liquid-vapor transitions near the hypercritical point. In our numerical works, spatial defects (impurities) have been placed on a diffusion limited cluster-cluster aggregate, which simulates the structure of silica aerogels. It is known that spatial correlations present a finite cut-off for this kind of disorder distribution. However numerical evidence has recently been presented that the 3DXY model confined within these objects presents a quite different critical behavior from bulk, and the numerical results agree well with reports on changes of criticality for superfluid 4He confined in silica aerogels. Such changes would violate theoretical criteria about the relevance of disorder on criticality. Fortunately, the results have been explained in terms of "hidden" long-range correlation within aerogels. On the other hand, Ising-type systems confined in aerogels also show interesting changes, quite different from random diluted Ising models studied in the past.

**4:15 PM *N6.5**
**Theoretical Studies of Chemistry in Nanoconfined Solvents.**
Ward H. Thompson, Chemistry, University of Kansas, Lawrence, Kansas.

Nanostructured materials have drawn increasing interest recently as potential vessels in which pools of solvent confined to nanoscale dimensions serve as an environment for chemical reactions. However, it is not clear what properties a confining framework should have in order to facilitate a desired reaction or hinder an undesired one. Theoretical studies will be presented that address the question How does a chemical reaction occur differently in a nanconfined solvent than a bulk solvent? In particular, chemical processes involving charge transfer (e.g., proton transfer reactions) that are intimately coupled to the solvent dynamics and thus exhibit pronounced changes upon confinement will be discussed. The effect of the confining framework properties on free energies, and dynamics will be examined.

**4:45 PM N6.6**
**Chemically Selective Reactions in Confined Spaces in Hybrid Aerogels.** Xipeng Liu, Chunhua Yao and William Risen, Jr.; Chemistry, Brown University, Providence, Rhode Island.

By employing novel hybrid silica/functional polymer aerogels, control of the course of chemical reactions between reactants confined inside of the aerogels with reactants whose access to the confinement domain is controlled by diffusion has been explored. Thus, monolithic silica/biopolymer hybrid aerogels have been synthesized with coordinated metal ions that can react with amino acids, such as L-cysteine, that are provided externally in a surrounding solution. Metal ions, such as Au(III), that can react in solution with the amino acid to produce one set of products under a given set of stoichiometric or concentration conditions, and a different set of products under a second set of conditions, were selected for incorporation into the aerogel. It was discovered that the course of the reaction can be changed by spatial confinement of the reaction domain in the aerogel. For example, in the case of Au(III) and L-cysteine, the Au(III) ions are confined in nanoscale domains, and when they are reacted with the amino acid the nature of the reaction products is controlled by diffusion of the L-cysteine into the domains. The concentration gradient-control of the diffusion thus serves to control the final product distribution. Exploration of these and related phenomena will be presented.

SESSION N7: Poster Session
Chairs: Pierre Levitz and Michael Urbakh
Wednesday Evening, November 30, 2005
8:00 PM
Exhibition Hall D (Hynes)

**N7.1**
**Effect of Nanostructure on the Thermal Oxidation of Atomized Iron.** Mohit Kumar[1], N. Rawat[1] and K. Santhanam[1];
[1]Center For Materials Science and Engineering, Rochester Institute of Technology, Rochester, NY, New York; [2]Department of Chemistry, Rochester Institute of Technology, Rochester, New York.

A number of theoretical studies have been carried out at understanding the interaction of transition metals with carbon nanotubes (1-6). An ab initio study of iron atom interacting with carbon nanotube suggested two possible types of interactions; in the first type of interaction iron atom is assumed to be interacting with the outside surface of the tube that is dependent on configurational geometry. In this case an effective configuration of 3d74s1 has been picturized. In the second type an iron atom is picturized as inside the tube resulting in a higher hybridization with effective configuration of 3d84so (1). As a result of quasi one dimensional face centered cubic structure of iron, this interaction inside the carbon nanotube favors the anti ferromagnetic ordering (2). Doping of transition metal atoms inside the carbon nanotube has also been considered theoretically for spintronic applications (3). Density functional calculations (4) suggests that iron atom adsorbing on hexagonal center of the nanotube as the most stable configuration with Fe-Fe distance of 2.23 Ao. The effect of nanostructure on the thermal oxidation of atomized iron has been investigated in this study. Atomized iron undergoes oxidation in the presence of air at temperatures above 520 C. However, when iron is compacted with multiwalled carbon nanotubes (MWCNT) this oxidation is shifted by more than 100 C. Iron is protected by the nanostructure environment similar to spintronics effect discussed earlier. A large number of compositions of atomic ratios of iron and MWCNT have been examined in this study by thermogravimetric analysis to understand the effect in detail. This oxidative temperature shift is absent with compacted iron-charcoal samples. It has been shown earlier (5) that the MWCNT shows a thermogravimetric transition at about 750 C. SEM and EDAX analysis were carried out to understand the nature of atomized iron at 600-800 C. The effect of nanostructure in the thermal oxidation of iron is interpreted as due to iron atom experiencing extensive overlap and confinement effect. Based on theoretical calculations reported in the literature this confinement effect of iron is suggested to produce a transformation of an effective configuration from 3d84so to 3d74s1.that results in spintronics. 1. Fagan, S. B., Mota, R., Physical Review B: 2003, 67(20), 2054 2. Fagan, S. B., Mota, R., Antonio J. R., Fazzio, A. Physica B: 2003. 3. Weissmann, M., Garcia, G., Kiwi, M., Ramirez, R. Physical Review B: 2004, 70(20), 201401 4. Yagi, Y., Briere, T. M., Sluiter, M. H. F., Kumar, V., Farajian, A. A.; Kawazoe, Y. Physical Review B 2004, 69(7), 5. Sangoi, R., Fuller, L., Santhanam, K. S. V. Mat. Res. Soc. Proc., Vol. 788, 2004 MRS, L10.4.1

**N7.2**
**Molecular Dynamics Studies of Surface Nucleation and Crystal Growth of Si on SiO2 Substrates.** Byoung-Min Lee[1],
Takahide Kuranaga[1], Shinji Munetoh[1], Hong Koo Baik[2] and Teruaki Motooka[1]; [1]Material Science and Engineering, Kyushu University, Fukuoka, Japan; [2]Metallurgical Engineering, Yonsei University, Seoul, South Korea.

Understanding the nucleation and crystal growth of Si on glass substrates in atomic scale is of great importance for improving performance of poly-Si thin film transistors. Although considerable information on the growth and properties of poly-Si films have been collected by using a variety of experimental techniques, it is still unclear how desirable textures and larger grains can be obtained during nucleation processes. In this study, we have investigated crystal growth of melted Si on SiO2 substrates using molecular dynamics simulations based on a combination of Langevin and Newtonian equations to deal with heat transfer from liquid Si to SiO2 substrates. The initial Si/SiO2 system was prepared by attaching a SiO2 substrate to c-Si. A new parameter set of the Tersoff potential was developed to calculate the interatomic forces of silicon and oxygen atoms. We find that the {111} plane of the nucleus is parallel to the surface. To investigate the origin of surface nucleation, we performed the calculations of surface energy based upon the number of bonds on the surface. The obtained surface energies are 2.27, 1.52, and 1.20 J/m2 for (100), (110), and (111) Si at 77 K, respectively, in good agreement with experimental results. These results suggest that, as the nucleus may be surface energy driven, the surface energy leads to a preferred (111) orientation of the Si thin films.

**N7.3**
**Nanoparticle-Reinforced Materials: Novel Design Concepts and Methods of Tailoring for Vibration Damping in Aerospace Components.** Maksim Kireitseu, [1]NAS of Belarus, Minsk, Belarus; [2]University of Sheffield, Sheffield, United Kingdom.

A novel concept of nanoparticle vibration damping [1, 2] shows the effect that molecule-level mechanism and friction can have on the damping and nanoparticles/fibres/tubes-reinforced materials can provide enhanced strength and vibration damping properties. It is particularly worth noting that carbon nanotubes and spider silk can act as a simple nanoscale spring with friction-related energy dissipation mechanism. The mechanisms involved in such materials need to be understood and the relevance to damping identified. Manufacturing design concept and modelling techniques for the next generation of vibration damping systems is largely unknown. The focus in this paper is directed toward to the investigation into carbon-based nanoparticle/fibre/tube-reinforced materials and coating systems and their dynamic/damping characterization. Computational

work will be concentrated on hierarchical multiscale modelling of damping/friction behaviour as a function of frequency, amplitude and temperature. A computational model is to be formulated in terms of meso- and nanoscopic ideas of damping behavior and could provide an approach to predict vibration damping properties and optimize some manufacturing design concepts of those material systems so as to enable the efficient synthesis of these novel materials. Cell-growth type models [3, 4] could be one way to achieve this. Systems that include statistical variation will be used to reduce the sensitivity "optimised" solutions to parameters. By establishing a strong linkage between the multidisciplinary sciences (physics, chemistry and mechanics), the proposed research will address both theoretical and applied aspects. The outcome of the project is expected to have wide-ranging technical benefits with direct relevance to industry in areas of transportation (aerospace, automotive, rail) and civil infrastructure development. However, the goal will be aerospace turbine applications and the next generation of fun blades. References 1. Rivera J.L., McCabe C., and Cummings P.T. Oscillatory Behavior of Double-Walled Nanotubes under Extension: A Simple Nanoscale Damped Spring. NANOLETTERS 2003, Vol. 3, No. 8, pp. 1001-1005 2. Li C. and Chou T.W. Single-walled carbon nanotubes as ultrahigh frequency nanomechanical resonators. Physical review B 68, 073405, 2003 3. Tomlinson G.R., Pritchard D and Wareing R, 2001, Damping characteristics of particle dampers - some preliminary results, Proceedings of I Mech E Part C, Vol 215, 253-257. 4. Tomlinson G R and Wardle R, 1996, A novel approach to structural design using biological models, ISMA 21 Conference, Structural Dynamics optimisation, Leuven, Belgium.

## N7.4
## Abstract Withdrawn

## N7.5
## Abstract Withdrawn

## N7.6
## Abstract Withdrawn

## N7.7
## Surface-Passivant Dependence of Dynamic Charging Effect in Alkanethiolate-Passivated Au Nanoparticles on Graphite Substrates Studied by Photoelectron Spectroscopy.
Akinori Tanaka, Masaki Imamura and Hidehiro Yasuda; Department of Mechanical Engineering, Kobe University, Kobe, Japan.

Photoemission study of Au nanoparticles surface-passivated by various alkanethiol molecules on the highly oriented pyrolytic graphite (HOPG) substrates, has been carried out in order to investigate their electronic structures and the nanoparticle-substrate interaction. From the detailed photoemission measurements, it is found that the Fermi-level onsets in the photoemission spectra of alkanethiolate- (AT-) passivated Au nanoparticles on the HOPG substrates are not the usual metallic Fermi edge, with the steep slope being away from the Fermi level. It is also found that the slopes of these leading edges depend on the surface-passivant molecules. These experimental photoemission spectra in the vicinity of the Fermi level are well characterized with a theoretical calculation that takes into account the influence of the photohole charging in the Au nanoparticle during the photoemission process and the nanoparticle-substrate interaction through the surface-passivants on a femtosecond timescale, so-called dynamic final-state effect model. In the case of photoemission, the nanoparticles are limited to have only positive charge (photohole), but the origin of this final-state effect on the photoemission process should be same as that of single-electron tunneling. Moreover, it is found that the obtained charging time of photohole from the dynamic final-state model calculation exponentially depends on the surface-passivant molecular length. This charging time of photohole directly corresponds to the tunneling time through the surface-passivants of AT molecules. Therefore, this surface-passivant dependence of photohole charging time is considered to reflect the tunneling resistance between the nanoparticle and substrate. From these results, we discuss the electronic structures and dynamic charging effect (dynamic final-state effect in photoemission) dominated by the nanoparticle-substrate interaction of AT-passivated Au nanoparticles on the HOPG substrates.

## N7.8
## Kinetics of Assembly and Equilibrium properties of Looped Brushes at the Solid-Liquid Interface. Jose Ernesto Alonzo and Michael Kilbey; Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina.

Dense layers of end-tethered polymers, often called polymer brushes, are of interest for their ability to modify interfacial properties. Along these lines, creating brushes comprised of loops by tethering the chains by both ends offers potential advantages in tailoring the adhesive or frictional properties of surfaces. Rigorously synthesized poly(2-vinylpyridine)-polystyrene-poly(2-vinylpyridine) triblock copolymers were used as a model system to examine the formation of looped brushes at the solid-liquid interface. In-situ phase modulated ellipsometry measurements were made to study the kinetics of assembly and equilibrium properties of these copolymers onto silicon surfaces. This technique allows the adsorbed amount and ellipsometric height of the layer to be sensitively measured as a function of time. These experiments provide evidence of looped brush formation: specifically, while the adsorbed amount increases asymptotically, the thickness shows an overshoot during the initial stages of adsorption followed by a slow reorganization. The final thickness of the looped brush is approximately one-half of that expected for a single-end tethered brush made from a diblock copolymer with a buoy block of similar molecular weight The equilibrium adsorbed amount and thicknesses follow well known scaling laws when each loop is considered as comprising two equal sized diblock copolymers. Considering this equivalent diblock model, the chains are stretched a few times their free solution radii of gyration. The effect of triblock molecular weight and composition on kinetics of layer assembly and structure, along with comparisons to those of diblock copolymers will also be presented and discussed.

## N7.9
## Switching Dynamics in Ferroelectric Polymer Nanomesas.
Christina M. Othon[1,2], Mengjun Bai[3], Jihee Kim[1,2], Stephen Ducharme[1,2] and Vladimir Fridkin[4,1,2]; [1]Physics and Astronomy, Univ. of Nebraska-Lincoln, Lincoln, Nebraska; [2]Center for Materials Research and Analysis, Lincoln, Nebraska; [3]Physics, Univ. of Missouri-Columbia, Columbia, Missouri; [4]Institute of Crystallography, Russian Academy of Sciences, Moscow, Russian Federation.

We have characterized the switching dynamics of ferroelectric nanomesas of poly(vinylidene-fluoride trifluoroethylene) 70:30 copolymer. Nanomesa films are formed by annealing Langmuir-Blodgett films thinner than 5 nm in the paraelectric phase. [1] The average height of the structures annealed at 135 °C are 10 nm, and have an average diameter of 80 nm. The nanomesas retain most of the ferroelectric properties of the bulk films, as has been shown by polarization measurements and x-ray diffraction. [1] We are reporting the first measurements of switching dynamics in these nanomesa structures with a switched charge of at least 20 mC/m$^2$, switching faster than 50 $\mu s$ , much faster than the average ultra thin Langmuir-Blodgett film of 1-100 s. [2] The nanomesas are promising structures for individual bits in a Non-Volatile Ferroelectric Random Access Memory (NV-FRAM). This work was supported by the USA National Science Foundation and the Nebraska Research Initiative. [1] M. Bai, et al., Appl. Phys. Lett. 85, 3528 (2004) [2] G. Vizdrik, et al. Phys. Rev. B 68, 094113 (2003)

## N7.10
## Low temperature melting of metallic nanorod arrays.
Tansel Karabacak, Pei-I Wang, Dexian Ye, Gwo-Ching Wang and Toh-Ming Lu; Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York.

We observed that tungsten, ruthenium, and copper nanorod arrays started melting at temperatures about ∼30-40 % of their bulk melting points. (Bulk melting temperature of W, Ru, and Cu are 3410 °C, 2334 °C, and 1083 °C, respectively). These findings reveal the most dramatic reduction in the melting temperature of nanostructures ever reported in literature. The nanorods were grown by an oblique angle sputter deposition technique through a physical self-assembly mechanism due to the shadowing effect. The W, Ru, and Cu nanorods had average widths of ∼75 nm, ∼75 nm, and ∼100 nm and average lengths of ∼500 nm, ∼370 nm, and 2300 nm, respectively. These nanorods were isolated from each other with gaps ∼20 nm. They were vacuum-annealed at various temperatures in the range of 300-1000 °C for 30 minutes at each annealing temperature. The melting process was investigated through the analysis of scanning electron microscopy images and X-ray diffraction spectra. W and Ru nanorods started to coalesce and formed continuous films at temperatures ∼1000 °C and ∼950 °C, respectively. After melting, W rods transformed from the metastable cubic $\beta$(200) phase to the bcc $\alpha$(110) phase and Ru rods changed their texture from hcp(100) to a mixture of (002) and (101) crystal orientations. Cu nanorods started to melt at ∼400 °C, and at ∼550 °C they coalesced and formed a dense continuous film with a (111) texture. Possible mechanisms that lead to the observed low temperature melting phenomena will be discussed. This work was supported by the NSF.

## N7.11
## Dynamics of Director Fluctuations in Confined Liquid Crystals. Sarmistha Basu, Edwin Arroyo and Fouad M. Aliev; Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

Dynamic light scattering was applied to study the influence of randomness as well of boundary conditions (planar-axial and

homeotropic-radial) and layer thickness (at nanoscale) of 5CB and 8CB confined to random porous matrices and to cylindrical pores on phase transitions and relaxation of director orientational fluctuations. For confined 8CB in the nematic phase two well-defined relaxation processes were observed for both axial and radial orientations of the liquid crystal. The first process is qualitatively associated with bulk-like nematic director fluctuations. The second relaxation process (with relaxation time slower than the first one) is most likely due to the fluctuations in layers nearest the wall surface. In samples with homeotropic boundary conditions we observed the onset of smectic-A phase order forming on the pore wall even though the rest of the liquid crystal could be in the nematic phase. We found that for homeotropic boundary conditions of confined liquid crystal, the pore wall-liquid crystal interactions influence on the properties of the surface layer is stronger than in the case of axial orientation, particularly, and the influence of boundary conditions on N-Sm-A phase transition in confined 8CB is stronger than on isotropic-nematic phase transition. The separation between the first and the second (slow) process is clearer for thinner layers and the amplitude of slow process is greater for thinner layers. This suggests that the slow process is surface related relaxation.

## N7.12
**Infrared Vibrational Spectra of tert-Butyl Halides in Low-Aluminum HY Faujasite. Vibrational Excitation Exchange and Other Effects of Guest-Host Interactions.**
Jack D. Fox, Research & Development, Rochester Midland Corporation, Rochester, New York.

Fourier transform infrared (FTIR) studies at 295 K of low-aluminum HY (LAHY, Si/Al = 40) faujasite supercage-included tert-butyl halides (CH3)3C-X (X = Cl, Br, I) are presented in comparison with the adsorbate molecular gas-phase and unloaded host solid-state spectra. The FTIR results, aided by computer modeling studies, reveal a propensity toward the exchange of quanta of vibrational excitation between guest modes and between guest and host modes. The exchange phenomenon along with C-H...O pseudo-hydrogen bonding effects are related to the siting of the guest molecules in the host supercages, and to the guest-host interactions at the guest sites.

## N7.13
**The Encounter Probability for Random Walkers in a Confined Space.** James P. Lavine, Image Sensor Solutions, Eastman Kodak Company, Rochester, New York.

Particles diffusing in a confined space should encounter one another with a probability that depends on the size and dimension of the space. This encounter probability is useful in predicting reaction rates in molecular systems [1] and in considerations of dark current in the pixels of solid-state image sensors [2]. The latter involves metal complexes such as copper pairs or a gold and iron complex in silicon. The dark-current generation rate is different for single atoms and pairs [3], hence, the interest in encounters. The present work uses random walkers on a lattice to investigate the encounter probability in one, two, and three spatial dimensions. The initial rapid decay of the survival-time distribution is nearly independent of the model space size. This stage is followed by an exponential decay in time, with a characteristic time that starts when the locations of the walkers have become randomized. The characteristic time is strongly dependent on the model space size L. For example, the characteristic time scales with L to the 2.06, the 2.31, and the 3.11 power in one, two, and three spatial dimensions, respectively. For a fixed L, the exponential tail of the survival time distribution has a similar slope when the initial separation of the two walkers is varied. The spacing between the exponential decay curves scales with the initial separation in 1-D, but not in 2-D or 3-D. The addition of a third random walker leads to a shorter characteristic time for the survival-time distribution, as is expected. The results from the present encounter problems will be compared to those from the study of reaction diffusion problems such as A + B goes to C [4]. In addition, the mapping of two random walkers to an equivalent single walker will be explored. 1. R.M. Noyes, J. Amer. Chem. Soc. 78, 5486(1956). 2. W.C. McColgin, J.P. Lavine, and C.V. Stancampiano, MRS Symp. Proc. 442, 187(1997). 3. K. Graff, Metal Impurities in Silicon-Device Fabrication (Springer , Berlin, 2000). 4. E. Monson and R. Kopelman, Phys. Rev. E69, 021103(2004).

## N7.14
**Development of a gas-selective carbon nanotube membrane.**
Jason K. Holt, Hyung Gyu Park, Aleksandr Noy and Olgica Bakajin; Biosecurity and Nanosciences Laboratory, Lawrence Livermore National Laboratory, Livermore, California.

Recent efforts have focused on the development of artificial membranes with nanoscale pores. Provided that the pore size can be well controlled at the length scale of molecular diameters, these membranes may find a wide range of applications from gas

separations (e.g. for use in CO2 sequestration) to ion exchange filters. Carbon nanotubes have inherent characteristics useful in fabricating size-controllable, high flux membranes, such as atomic smoothness and nanometer-scale diameters. Multiwall carbon nanotube/silicon nitride membranes have been developed that exhibit pore sizes of order 7 nm, a size scale above which molecular sieving effects or deviations from rarefied Knudsen diffusion are predicted. Measurements recently conducted, however, indicate deviations from the linear flux/pressure drop relation expected for Knudsen diffusion. A discussion of these results in the context of flow through packed beds will be presented. Another novel feature of these membranes is a reduced permeability of select gases, due perhaps to molecule-surface interactions. The ultimate aim is to develop a single wall carbon nanotube membrane, for which gas selectivity and high flux should be achievable. Recent results on the fabrication of such membranes will be presented.

## N7.15
**Morphology and mechanical properties of helical carbon nanofibers synthesized by chemical vapour deposition.** Yong Qin, Ruijiang Hong and Xin Jiang; Institute of Materials Engineering, Siegen University, Siegen, Germany.

Novel helical carbon nanofibers were synthesized on copper nanocrystals by chemical vapour deposition using $C_2H_2$ as a precursor gas at a low temperature of 250 $^0$C. The morphology, microstructure, and mechanical properties of the obtained helical nanofibers were characterized by means of scanning electron microscope, transmission electron microscope, Raman spectrometer and nano indenter, respectively. The following are the findings: The nanofibers are regularly coiled with a coil diameter of about 80 nm. There are always two helical nanofibers growing from a single copper nanocrystal, consequently showing a symmetrical growth mode in the form of twin-helixes. The two helical nanofibers have identical morphologies except for different helical senses. These nanofibers have an amorphous structure because of the low deposition temperature. They possess good elasticity and present interesting processable properties.

## N7.16
**Conformational Studies Of Responsive Weak Polyelectrolyte Brushes.** Andrew John Parnell[1], Richard A. L. Jones[1], Mark Geoghegan[1] and Anthony J. Ryan[2]; [1]Physics and Astronomy, University of Sheffield, Sheffield, United Kingdom; [2]Chemistry, University of Sheffield, Sheffield, United Kingdom.

The area of soft nanotechnology requires the development of smart polymer systems capable of responding to changes in external stimuli. Weak Polyelectrolyte brushes are an excellent example of such a system as they are capable of respondng to changes in pH. We have succeeded in developing synthesis routes for creating well-defined chemically grafted, weak polyacid and polybase polymer brushes at high grafting density and good surface uniformity using atom transfer radical polymerization. This polymerization technique has made it possible to examine systematically the response of these brushes to changes in their environment. Neutron reflectivity experiments have shown that the poly(diethylaminoethyl methacrylate) and poly(methacrylic acid) brushes swell in response to changes in the pH of the sub-phase. Atomic force microscopy (AFM) studies of the total thickness have been performed to examine the dynamics in response to pH change as well as the more complex addition of added salt ions and valence of the added salt ion. AFM has also shown the real time swelling and de-swelling of a poly(methacrylic acid) brush as the pH is switched. Single molecule force spectroscopy has highlighted distinct behaviour differences between collapsed and expanded brush states. As well determining the molecular weight and persistence length of our brushes. Brushes like these may find important applications in technologies where pH responsive behaviour is particularly desirable such as in controlled drug delivery.

## N7.17
**Non-Linear Analysis of Electromigration-Induced Surface Waves on Voids Confined in Metallic Thin Films.** Jaeseol Cho, M. Rauf Gungor and Dimitrios Maroudas; Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts.

Electromigration-driven void evolution in metallic thin films has been a problem of major interest both as an important interconnect reliability concern in integrated circuits, where void defects are confined within fine-scale features, and as an intriguing nonlinear dynamical mechanism of microstructural evolution. In this presentation, we focus on the analysis of electromigration-induced waves on void surfaces and their implications for the metallic line electrical properties. The analysis is based on self-consistent numerical simulations of current-induced morphological evolution of void surfaces in metallic thin films. The mass transport problem on the void surface is solved coupled with the electric field distribution in the conducting film that contains the morphologically evolving void. Current crowding in the narrow metallic films, a strong effect of

confinement, and the strong anisotropy of adatom diffusion are accounted for rigorously in the simulations. The analysis predicts the onset of stable time-periodic states for the void surface morphological response as either the applied electric field strength, or the void size, or the strength of the diffusional anisotropy is increased over a critical value. For parameter values below the critical ones, morphological evolution leads to stable steady states for the void surface morphology; these steady states correspond to morphologically stable voids that translate along the metallic film at constant speeds (i.e., solitons). It is demonstrated that the different sequences of morphological transitions and instabilities as different operating conditions and system parameters are varied correspond to either supercritical or subcritical Hopf bifurcations. To compare our theoretical predictions with experimental data, the effects of void dynamics under electromigration conditions on the metallic film's electrical resistance, a readily accessible experimental parameter, are considered and the electrical resistance evolution is calculated. Changes in the metallic line resistance are found to depend strongly on electromigration-induced void morphological changes. In particular, propagation of stable time-periodic surface waves is found to give rise to stable time-periodic electrical resistance response. The theoretical results provide interpretations for experimental measurements that have demonstrated stable oscillatory dynamics in the electrical resistance evolution of metallic interconnect lines.

## N7.18
**Effects of Elastic Stress on Electromigration-Driven Dynamics of Voids Confined in Metallic Thin Films.** M. Rauf Gungor, Vivek Tomar and Dimitrios Maroudas; Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts.

Relaxation of thermomechanical and electromigration-induced stresses through nucleation and evolution of voids in metallic thin films has been a problem of major interest due to interconnect reliability concerns in microelectronics, as well as a fundamentally interesting problem of driven microstructural dynamics. By employing both atomistic and continuum methods, recent theoretical work on this problem has demonstrated the growth, morphological evolution, and surface morphological instability of voids that may lead to failure of the metallic thin films that confine them driven by electromigration, stress-induced surface diffusion, and elastoplastic deformation. In this presentation, we focus on the analysis of the effects of biaxially applied elastic stress on the migration of stable voids in metallic thin films. Our theoretical analysis is based on self-consistent numerical simulations of current- and stress-induced void migration and morphological evolution. The simulations account rigorously for current crowding and stress concentration in narrow metallic films with voids, which are strong confinement effects, as well as the strong anisotropy of adatom diffusion on void surfaces. Contrary to the common belief that the effects of elastic stress are generally catastrophic on the stability of void surface morphology, we demonstrate that under certain surface diffusion anisotropy, plane-strain mechanical loading, and electromigration conditions, there is an applied stress range that stabilizes the void morphological response, which would be unstable without the application of stress. We present results of linear stability analysis of void morphological evolution under the combined driving forces of capillarity, elastic stress, and electromigration and use them to discuss the findings of our numerical simulations. In addition, we demonstrate, again contrary to common belief, significant effects on the electromigration-induced stable void migration of mechanical stress application in a metallic thin film. Specifically, we find that under certain electromechanical conditions, elastic stress can cause substantial retardation of void motion, as measured by the constant speed of electromigration-induced translation of morphologically stable voids. More importantly, this effect suggests the possibility for complete inhibition of void motion under stress.

## N7.19
**Theory of Slope-dependent Disjoining Pressure with Application to Lennard-Jones Liquid Films.** Taeil Yi and Harris Wong; Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana.

A molecule in a bulk liquid is subject to intermolecular forces. A molecule in a thin liquid film may experience additional intermolecular forces if the film thickness h is less than approximately 100 nm. The additional forces arise from the molecule's proximity to different materials or phases sandwiching the thin film. The effect of these intermolecular forces at the continuum level is captured by disjoining pressure P. Since P dominates at small film thicknesses, it determines the stability and wettability of thin films. To leading order, $P = P(h)$ because thin films are generally uniform. This form, however, cannot be applied to films that end at the substrate with non-zero contact angles. We have developed a new procedure for deriving new disjoining-pressure expressions that depend on the film slope hx as well as the film height h.[1] In this approach, the total energy of a drop on a solid substrate is minimized. The minimization yields an equilibrium equation that relates P to an excess interaction energy $E = E(h, hx)$. By considering a fluid wedge on a solid substrate, $E(h, hx)$ is found by pairwise summation of van der Waals potentials. This yields $P = P(h, hx, hxx)$. The current work extends the summation to the Lennard-Jones potential. We find again $P = P(h, hx, hxx)$, but the new expression accepts a much larger class of equilibrium drop and meniscus shapes, including a drop with a finite precursor film, and two drops connected by a precursor film. These new drop profiles have been observed in experiments but have not been predicted by previous disjoining pressure models. [1] Wu & Wong, J. Fluid Mech. 506, 157-185 (2004).

## N7.20
**Simulation of Transport Properties of Rare Gas Liquid in Confinements.** Yoshiaki Kogure, Teikyo Univ. of Science & Technology, Uenohara, Yamanashi, Japan.

A molecular dynamics simulation for transport properties of rare gas liquid confined in nanospaces has been performed. The system is consisted of ten thousand atoms interacting by the Lennard-Jones potential and confined in tubes of several nanometers in diameter and the dozens of nanometer in length. The boundary of the tube is consisted of fixed atoms of same species, namely, of same potential parameters. The flow of atomic system in the tube is simulated as functions of the particle density and the temperature. The process of evolution of steady flow in the tube is monitored by the trajectory of atoms. Atomistic diffusion, and the capillary motion of atoms under pressure are calculated from the displacement and velocity data of the atoms. Then, the transport coefficient, the viscosity and the diffusion coefficient, of the liquid is evaluated as a function of temperature. Present method of simulation could be a fundamental approach to investigate the capillary motion of water molecule in the soil or the dynamics of body fluid in the living body systems.

## N7.21
**Simulation Study of Confinement Effects on the Melting Transition in Hexane and Decane Monolayers Between Two Graphite Slabs.** Cary L. Pint and Michael W. Roth; Physics, University of Northern Iowa, Cedar Falls, Iowa.

At the interface between two solid surfaces, it is well known that a single thin layer of a lubricant can reduce the dissipated energy between the surfaces due to friction, and can reduce the wear resulting on the surfaces from interaction. However, when one imposes confinement upon the lubricating layer, the dynamics that describe the phases and how the phase transitions take place are expected to change significantly, as will be demonstrated in this study. In this work, a molecular dynamics (MD) method is utilized to study the melting transition in ultrathin hexane ($C_6H_{12}$) and decane ($C_{10}H_{22}$) monolayers confined at the interface between two graphite surfaces. The $n$-alkanes are specifically chosen due to their well-known properties as lubricants, which warrants their use in many industrial and commercial applications that involve lubrication on the surface. In order to characterize the melting behavior and the induced changes due to confinement, several temperature points are simulated for each monolayer at graphite wall separations (GWS) ranging from 6-20Å, with 18 total different GWS studied. To model the alkane molecules, a simple united-atom (UA) approach is utilized which seems to be well in agreement with experimental observations for both solid monolayers studied in this work. Hexane and decane monolayers are chosen due to recent work which studies their melting behavior on a single graphite surface, without confinement. Monolayers of hexane are found to melt through a tilting mechanism, where decane monolayers are found to melting via the formation of gauche defects in the molecule chains, each satisfying the footprint reduction previously proposed by Hansen et al. The difference in the melting mechanism for these single physisorbed monolayers provides the motivation for comparison of these two monolayers in confinement. There seem to be similarities in the melting behavior of these monolayers as the GWS is increased. Near a spacing of 10Å, both confined monolayers seem to indicate a melting temperature that is within ca. 15-20% of the solid monolayer melting temperature without confinement. However, at closer GWS, the melting temperature raises drastically due to the increased interaction of the adsorbate with the corrugation in the top surface. Also, the presence of layer promotion in the confined hexane monolayer seems to appear at a GWS of ca. 14Å, indicating a GWS threshold by which the interaction energy can by minimized through layer promotion in the presence of confinement. In general, by a GWS of 20Å, there seems to be little effect on the adsorbate layer from the interaction of the top graphite wall for both simulated monolayers. Thus, this work gives a broad understanding of the solid-fluid phase transitions for confined lubricating monolayers, which could have many implications toward an understanding of boundary lubrication and related phenomena.

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**N7.22**
**Hole Dynamics in Polymer Langmuir Films.** Lu Zou[1], Andrew J. Bernoff[4], James A. Alexander[2], J. Adin Mann[3] and Elizabeth K. Mann[1]; [1]Physics, Kent State University, Kent, Ohio; [2]Mathematics, Case Western Reserve University, Cleveland, Ohio; [3]Chemical Engineering, Case Western Reserve University, Cleveland, Ohio; [4]Mathematics, Harvey Mudd College, Claremont, California.

This article develops a model for the closing of a gaseous hole in a liquid domain within a two-dimensional fluid layer, coupled to a fluid bulk substrate, and compares this model to experiments following hole dynamics in a polymer Langmuir monolayer. Closure of such a hole in a fluid layer is driven by the difference in pressure within the hole and far outside it, and by the line tension. The observed rate of hole closing is close to that predicted by our model and the line tension measured by other means, assuming that the pressure in the gas is negligible. This result both supports the model and suggests an independent means of determining the line tension. Unlike most previous hydrodynamics models of Langmuir films, the closing of a hole necessarily invloves vertical motion of the underlying incompressible fluid: that fluid is dragged along with the liquid monolayer towards the center of the hole, and must plunge away from the surface. An explicit expression is found for this vertical fluid flow in the bulk substrate. This material is partially based upon work supported by the National Science Foundation under Grant No.9984304.

**N7.23**
**Translational and Rotation Diffusion of Individual Single-Walled Carbon Nanotubes Studied with Fluorescent Microscopy.** Sergei M. Bachilo[1,2], Dmitri A. Tsyboulski[1,2] and R. Bruce Weisman[1,2]; [1]Chemistry, Rice University, Houston, Texas; [2]Center for Biological and EnVironmental Nanotechnology, Rice University, Houston, Texas.

Single-walled carbon nanotubes (SWNT) exhibit intrinsic photoluminescence [1], and fluorescent microscopy can be used to observe individual nanotube macromolecules [2]. In the present work, results of dynamic observation of SWNT motion in liquid media are presented. Unmodified SWNT were studied using a fluorescent microscope with a NIR camera. Translation diffusion was defined from direct observation of a nanotube position at different times. For resolution of rotational motion, intensity of fluorescence at different times was measured. Due to high anisotropy of absorption, which is determined by a transition being linearly-polarized along the nanotube axes, the excitation depends on angle between the nanotube axes and the polarization of excitation laser light. Analyzing the intensity variation, we determined rotational diffusion parameters of individual nanotubes. Both diffusion parameters, defined concurrently for individual nanotube macromolecules, were used to calculate spatial characteristics, such as length and efficient diameter, for SWNT in various environments. Different conditions include SWNT covered with a surfactant layer and SWNT interacting with polymeric and biopolymeric molecules in water. [1] M.J. O'Connell et al, Science 297 (2002), 593 - 596 [2] D.A Tsyboulski et al, Nanoletters 5 (2005), 975 - 979

**N7.24**
**Langmuir Layers of Bent-Core Liquid Crystals.** Ji Wang[1], Lu Zou[1], Antal Jakli[2], Wolfgang Weissflog[3] and Elizabeth K. Mann[1]; [1]Physics, Kent State University, Kent, Ohio; [2]Liquid Crystal Institute, Kent State University, Kent, Ohio; [3]Institut fur Physikalische Chemie, Martin-Luther-Universitat Halle-Wittenberg, Halle, Germany.

Bent-core liquid crystals are confined at the air/water interface. They form discretely layered structures even where the material does not form smectic liquid crystals in bulk samples. Structure and phase transitions are characterized by X-ray diffraction, surface pressure, Brewster angle microscopy, x-ray, and surface potential measurements. Optical anisotropy allows us to determine the tilt angle with respect to the film normal and to domain features, as well as the refractive index anisotropy. This material is based upon work supported by the National Science Foundation under Grant No.9984304. The surface potential work was supported by the Petroleum Research Fund, under grant ACS PRF# 35293-G 7. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No W-31-109-Eng-38.

**N7.25**
**Diameter-Dependence of the Radial-Breathing Frequency in Carbon Nanotubes and Its Relation to Properties of Bulk Graphite.** Hadley Lawler[1], Carter T. White[1] and John W. Mintmire[2]; [1]US Naval Research Laboratory, Washington DC, District of Columbia; [2]Department of Physics, Oklahoma State University, Stillwater, Oklahoma.

When a graphite sheet is rolled to form a carbon nanotube, there is a mapping between bulk, elastic properties and "optical" excitations in the nanostructure. In particular, the parameters entering elastic in-plane bond stretching are related to the diameter dependence of the radial-breathing frequency in the nanotubes, and can be compared. Thus, the strong enhancement of the radial frequency with increased confinement and decreased diameter can be directly related to the bulk elastic property. Furthermore, the curvature energy, which is pertinent to the measurable quadratic dispersion of the ZA phonon in bulk graphitic systems, ought also to contribute to the variation of radial-breathing frequency with diameter. We relate these perspectives to our first-principles calculations of the radial-breathing frequency for all carbon nanotubes in the diameter range 0.4 to 1.4 nm.

**N7.26**
**Mapping Dynamics of Stability of Thin Polymer Films: Surface Energy and Temperature Effect.** Karen M. Ashley[2], Dharmraj Raghavan[2], Jack F. Douglas[1] and Alamgir Karim[1]; [1]Polymers Division, NIST, Gaithersburg, Maryland; [2]Chemistry, Howard University, Washington D.C., District of Columbia.

We have mapped a film stability line governing the transition between wetting and dewetting in ultrathin polymer films as a function of temperature and surface energy. To this end, we construct image maps of wetting / non-wetting regions of polystyrene (PS) films cast on substrates having orthogonal temperature and surface energy gradients. Qualitative analysis of contact angle of dewet droplets below the instability line is consistent with the morphological phase map data. A series of measurements are performed for a range of molecular masses (1,800 g/mol < M < 35,000 g/mol) and film thicknesses h (30 nm < h < 40 nm) to explore these primary parameter-space axes. We find that the effective polymer surface tension becomes appreciably modified in polymer films thinner than about 100 nm to 200 nm, so that bulk surface tension measurements cannot be used to estimate the stability of ultrathin films. We also obtain a near-universal scaling curve describing a wetting-dewetting transition line for polystyrene films of fixed thickness by introducing reduced temperature and surface energy variables dependent on M. Surprisingly, elevated temperature experiments show a lack of sensitivity of thin film stability to temperature, in contrast to the appreciable temperature dependence of bulk surface tension in this temperature range. The dynamics of evolution of the stability line in these nanometer thick films and implications for modification of polymer-substrate interactions in glassy films will be discussed. These observations are potentially fundamental for the control of thin film stability in applications where film dewetting can compromise film function.

**N7.27**
**Abstract Withdrawn**

**N7.28**
**Abstract Withdrawn**

**N7.29**
**Sliplink Simulations of Entangled Polymer Dynamics.** Scott Milner, ExxonMobil, Annandale, New Jersey.

Recent progress on stress relaxation of entangled branched polymers in linear response, has led to reexamination and refinement of the responsible mechanisms (reptation, arm retraction, contour length fluctuations, constraint release). This has led to yet more recent progress on stress relaxation of entangled linear polymers in the nonlinear regime, with one additional mechanism (convective constraint release). Simulations based on sliplink dynamics have proven tractable and reasonably accurate in capturing the nonlinear dynamics of entangled melts. I will illustrate this with several examples, including stress upon startup and cessation of steady shear, as well as self-diffusion of bidisperse chains.

**N7.30**
**Nano-Thermometry of Confined Free-Standing Thin Films During High Intensity Ultrafast Laser Interaction with Si.** Yoosuf N. Picard[1], Ben Torralva[2] and Steven Yalisove[1]; [1]Materials Science & Engineering, Univ. of Michigan–Ann Arbor, Ann Arbor, Michigan; [2]Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, California.

It has been shown that the use of ultrafast lasers for controlled micro- and nano-scale machining has favorable advantages over longer pulse length lasers. Minimal heat dissipation is one often cited advantage, allowing for more controlled machining at smaller length scales approaching tens of nanometers. However, the actual probing of this heat dissipation outside the actual area of laser irradiation has been limited to the 10-100 micron scale. The dynamics of the region immediately adjacent to the hole produced by laser machining has

never been studied. Theoretical studies have suggested that the region confined to 200 nm from the hole edge experiences high pressures and high temperatures. Furthermore, these regions are predicted to have extremely high thermal gradients. We will present our first results to measure the thermal gradients on the nanoscale with ~20 nm precision. In this study, we have deposited silicon/cobalt thin films on a silicon substrate at room temperature in ultra high vacuum, and then laser irradiated the multilayer system. Using plan-view transmission electron microscopy, we have probed the holes generated by single pulse laser machining and the resultant microstructure as a function of distance away from the hole. By observance of the phase changes resulting from the laser machining, we can determine a maximum temperature profile both inside and outside the area of laser irradiation. Hydrodynamic calculations will be presented that provide insight into the dynamics responsible for confinement of the thermal load.

## N7.31
**Effect of Surface Ion Distributions on the Mobility of Single Dye Molecules on MICA.** Arne Schob and Frank Cichos; Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany.

The interaction of a liquid with a solid surface is in part determined by the detailed surface chemistry of the solid. A heterogeneous surface which provides a variety of adsorption sites will lead to an overall complex interaction of liquid molecules with the surface and thus also induce locally different dynamics of the liquid at the interface. The details of this interaction are of great importance for a number of processes including the study of confined liquids e.g. in a surface forces apparatus. By studying the diffusion of single dye molecules in a thin liquid film at a freshly cleaved MICA surface, we find evidence for different local ion distributions between different cleaving surfaces. Regions of slow and fast molecular mobility are found together with complete dewetting of the liquid at certain parts of the surface. The difference in mobility is strongly related to the ionic nature of dye molecules as demonstrated by the use of different dye molecules. The importance of ion distributions is further supported by wetting experiments, which show instabilities of the three phase contact line due to an accumulation of charges.

## N7.32
**A Surface Forces Apparatus for Single Molecule Tracking.** Arne Schob and Frank Cichos; Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany.

A surface forces apparatus (sfa) is a well-established technique to study liquid-solid interactions in ultrathin confined films on mesoscopic length scales. Shear experiments within a sfa can help understanding friction with ultrathin lubricant layers more detailed although a conventional sfa is limited to ensemble the effect in the ensemble of liquid molecules in the confined film. Spatial variations of the liquids dynamics are essentially hidden in these experiments even though they should exist. Tracking of single molecules could thus be of tremendous benefit here, because anisotropies and inhomogeneities of the molecular diffusion can be easily revealed. For the first time we present a surface forces apparatus, which has been modified to provide access to molecular motion within confined liquids using a tracking of single fluorescent molecules. Force-distance-curves of our setup demonstrate that a capacitive position sensor is able to replace the common interferometric thickness measurement, even though the sensor is placed outside the confined region. With the help of this setup we evaluate the molecular mobility of dye molecules in a thin film confined film of tetrakis(2-ethyhexoxy)silane. A dependence of the diffusion constant on the thickness is presented. With a separation of external force driven motion (shear) from stochastic driven diffusion we even demonstrate the possibility to investigate molecular details of confined liquids under shear, which may serve as a model for ultrathin lubricant layers between solid surfaces.

## N7.33
**The Thermal Stability of Imprinted Polymer Nanostructures.** Christopher L. Soles[1], Ronald L. Jones[1], Hyun Wook Ro[1], Eric K. Lin[1], Alamgir Karim[1], Wen-li Wu[1], Walter Hu[2] and Stella W. Pang[2]; [1]Polymers Division, NIST, Gaithersburg, Maryland; [2]Department of Electrical and Computer Science Engineering, University of Michigan, Ann Arbor,, Michigan.

Nanoimprint lithography is used to fabricate parallel line and space gratings in poly(methyl methacrylate) (PMMA) films. Under elevated temperature and pressure the viscous PMMA flows into the sub-100 nm line-space cavities of the imprint mold, leaving an impression of the grating in the film when the mold is cooled to room temperature and pulled away from the film. We illustrate here that these imprinted structures retain significant levels of residual stress, induced by the shear fields as the viscous PMMA flows into the mold. Critical dimension small angle X-ray scattering and specular X-ray reflectivity are used to quantify the periodicity of the gratings, the average line width, average line height and the sidewall angle of the trapezoidal cross sections of the lines. The imprints are then annealed near the glass transition temperature of the PMMA where the patterns begin to change their shape. The periodicity of the gratings does not change with annealing, but the line height decreases, the line width broadens, and the sidewall angles of the trapezoidal cross-section broadens. This shape evolution is described as a melting or slumping of the patterns. However, in the early stages of annealing the patterns reduce their height at a rate that is one to two orders of magnitude faster than the rate at which they broaden in width. Surprisingly, these rates of pattern change increase as the molecular mass of the PMMA increase, contradicting a viscous flow mechanism for the pattern slumping. Rather, the pattern slumping (at least at short times) is driven by the residual stresses in the nanostructures that are created by the shear fields as the viscous polymer is forced into the small mold cavities; in the short duration of the imprint process the flow induced shear stresses do not have time to sufficiently relax. With this mechanism the higher molecular mass PMMA would have a larger viscosity, larger shear stresses, greater residual stresses, and therefore the faster pattern slumping rate at least until the residual stresses are fully relaxed.

## N7.34
**Molecular Relaxation Dynamics of Self-Assembled Monolayers.** Qing Zhang and Lynden Archer; Chemical Engineering, Cornell University, Ithaca, New York.

This work reports the first quantitative study of molecular relaxation dynamics in self-assembled monolayers (SAMs). Dielectric spectroscopy is used to investigate relaxation dynamics of alkylsilane SAMs on porous glass. A relaxation process with activation energy ~25kJ/mol is found to dominate dynamics of molecular segments near the substrate. By introducing polar CN groups at the chain ends we show that relaxation process in the monolayer canopy can be isolated and studied. Our approach can be generalized to other substituent polar groups to probe localized relaxation dynamics in monolayers.

## N7.35
**Abstract Withdrawn**

## N7.36
**Preparing Uniform Conducting Polymer Nanoparticles and Nanorods in Dynamic Microfluidics.** Karla Coti[2], Weixing Lu[1], Guodong Sui[1] and Hsian-Rong Tseng[1]; [1]Crump Institute for Molecular Imaging and Department of Molecular and Medical Pharmacology, David Geffen School of Medicine at UCLA, Los Angeles, California; [2]Department of Chemistry and Biochemistry, UCLA, Los Angeles, California.

In this presentation, we describe a proof-of-concept experiment, in which conductive polymer-based nanoparticles and nanorods are prepared in a dynamic nanoenvironment with precisely controlled morphologies. Such a dynamic nanoenvironment is created in PDMS-based microfluidic channels, where a number of lamellar streams containing monomer precursors and oxidants were confined within a nanometer region through hydrodynamic focusing. The monomers and oxidants in the respective streams are mixed through the diffusion within microseconds (ms). Meanwhile, the monomer precursors are polymerized and crystallized within this nanoenvironment. The sizes of the nanoparticles and nanorods can be controlled by varying the thickness of lamellar streams. These results not only constitute a proof of principle for synthesizing of conducting polymer nanoparticles and nanorods in a dynamic nanoenvironment but also provide the impetus to employ hydrodynamic focusing for the preparation of nanostructured materials in microfluidic systems.

## N7.37
**Nanobubble Formation at the Solid-Liquid Interface Studied by Atomic Force Microscopy.** Abhinandan Agrawal and Gareth H. McKinley; Hatsopoulos Microfluids Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The formation of nanobubbles at solid-liquid interfaces has been studied using the atomic force microscopy (AFM) imaging technique. Nanobubble formation strongly depends on both the hydrophobicity of the solid surface and the polarity of the liquid subphase. While nanobubbles do not form on flat hydrophilic (silicon oxide wafer) surfaces immersed in water, they appear spontaneously at the interface of water against smooth, hydrophobic (silanized wafer) surfaces. From the experimental observations we draw the conclusion that the features observed in the AFM images are deformable, air-filled bubbles. In addition to the hydrophobicity of the solid surface, differences in solubility of air between two miscible fluids can also lead to formation of nanobubbles. We observe that nanobubbles appear at the interface of water against hydrophilic silicon oxide surfaces after in-situ mixing of ethanol and water in the fluid-cell. The

shapes of the nanobubbles are well approximated by spherical caps, with width much larger than the height of the caps. We quantify the morphological distribution of nanobubbles by evaluating several important bubble parameters including surface coverage and radii of curvature. In conjunction, with an analytical model available in the literature, we use this information to estimate that the present nanobubble morphology may give rise to slip lengths of $\sim$1−2 $\mu$m in pressure driven flows for water flowing over the hydrophobic surface. The consistency of the calculated slip length with the experimental values reported in the literature, suggests that the apparent fluid slip observed experimentally at hydrophobic surfaces may arise from the presence of nanobubbles.

### N7.38
**Enhanced Biodetection and Enzymatic Reaction Using Microelectrodes.** Siu-Tung Yau and Gang Wang; Physics, Hunter College of City University of New York, New York, New York.

A systematic study of enzymatic reaction of glucose oxidase (GOx) immobilized on microelectrodes of decreasing size is presented. Detection of glucose using the electrodes was achieved by monitoring the reduction current of the immobilized GOx assembly. The signal-to-background ratio has a highly nonlinear dependence on the electrode area, showing enhanced detection due to suppression of electrode capacitance. Detection limit as low as 500 nano-molar was obtained. The calibration curves of the electrodes show the typical Michaelis-Menten (M-M) characteristic. The kinetic parameters of the GOx assemblies were found to scale down with the electrode size, making the enzymatic reaction more effective. The decreasing values of the kinetic parameters are related to the special characteristics of mass transport for microelectrodes. An additional cause for the enhanced detection, which involves the electrode-size dependent kinetics, is proposed.

### N7.39
**Mobility of DNA on Supported Lipid Bilayers.**
Chakradhar Padala[1], Richard Cole[2], Sanat Kumar[1] and Ravi Kane[1]; [1]Chemical & Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York; [2]Wadsworth Center, NYS Department of Health, Albany, New York.

The study of the dynamics of biopolymers such as DNA at interfaces is not only of fundamental interest but also useful in the development of biosensors and novel DNA separation strategies. In this work, we investigate the mobility of DNA adsorbed onto supported lipid bilayers. DNA was adsorbed onto a supported lipid bilayer whose mobility could be tuned by varying the temperature. Fluorescence Recovery after photo bleaching (FRAP) was used to determine the diffusivities of the lipid and that of DNA adsorbed on the bilayer. FRAP analysis reveals an interesting interplay between the mobility of the substrate and the mobility of the DNA. We will discuss these results, as well as results for DNA diffusion on solid surfaces.

### N7.40
**Abstract Withdrawn**

SESSION N8
Chair: Amit Meller
Thursday Morning, December 1, 2005
Room 202 (Hynes)

**8:30 AM *N8.1**
**Equilibrium and Out-Of-Equilibrium Behavior of Fluids in Disorderd Porous Materials: The Case of Silica Aerogels.**
Francois Detcheverry, Martin-Luc Rosinberg, Gilles Tarjus and Edouard Kierlik; Lab. Physique Theorique de la Matiere Condensee, Universite Pierre et Marie Curie, Paris, France.

The adsorption of gases in mesoporous materials is generally described in terms of capillary condensation, the abrupt filling of the pore volume by the liquid phase. Usually, hysteresis is observed in sorption isotherms as desorption proceeds differently than adsorption. Although isotherms are widely used for characterizing porous materials, their interpretation remains controversial. None of the standard approaches proposed in the litterature, either modeling the solid as a collection of independant pores of simple geometry but varying sizes (i.e. Preisach model) or focusing on kinetic network effects can reproduce altogether the experimental observations. In this talk, I will summarize recent works carried out by our group in Paris. We propose a unifying theoretical framework based on a coarse-grained description of fluids in disordered solids. The model contains the essential physical ingredients that characterize such systems: confinement, randomness of the pore network and wettability of the solid surface. Applying a local mean-field theory, a detailed investigation of the equilibrium and out-of equilibrium (hysteretic)

properties of a model of silica aerogels at various porosities [1] and temperatures [2] shows that - hysteresis can occur both with or without a true equilibrium transition. - the morphology of the hysteresis loops is affected by out-of-equilibrium phase transitions that differ on adsorption and desorption and which present similarities with those observed in low-temperature ferromagnetic materials. - The filling process occurs via avalanches, i.e. irreversible condensation events whose shapes and sizes display a great variety with porosity an temperature. In high porosity gels at low temperature, avalanches may be macroscopic and the adsorption isotherms exhibit a sharp transition. - Desorption may proceed via two different mechanisms : appeareance and growth of bubbles of gas in the bulk of the porous material or the motion of the liquid-gas interface from the boundaries of the sample. The gas invasion may be either continuous with an interface which penetrates in a fractal-like structure the solid, or discontinuous as the interface suddenly sweeps through the whole sample. [1] {Local mean-field study of capillary condensation in silica aerogels}, F. Detcheverry, E. Kierlik, M. L. Rosinberg and G. Tarjus, Phys. Rev. E {68}, 061504 (2003). [2] {Mechanisms for gas asorption an desorption in silica aerogels : the effect of temperature}, F. Detcheverry, E. Kierlik, M. L. Rosinberg and G. Tarjus, Langmuir {20} (19), 8006-8014 (2004).

**9:00 AM *N8.2**
**Relation Between Structure and Diffusion in Nanostructured Porous Solids and in Lipid Membranes.** Sergey Vasenkov and Joerg Kaerger; Physics, Leipzig University, Leipzig, Germany.

Recent advances in microscopic techniques, which are capable of monitoring molecular diffusion on nanometer and micrometer length scales, opened a direct way to study relation between structure and transport in nanostructured materials. These materials can be as diverse as hierarchically organized porous catalysts and lipid membranes. Progress in the area of the pulsed field gradient (PFG) NMR technique has made possible the direct measurement of diffusivities in fluid catalytic cracking (FCC) catalysts, which present an example of hierarchical porous system. This is demonstrated in the present work. The diffusivities recorded on various length scales are used to evaluate the relevance of various transport modes in the particles of FCC catalysts, such as diffusion in the micropores of the zeolite crystals located in the particles, diffusion through the surface layer of these crystals and diffusion in the meso- and macropores of the particles, for the rate of molecular exchange between catalyst particles and the surrounding atmosphere. This rate is shown to be primarily related to the diffusion in the meso- and macropores of the particles under the condition of fast molecular exchange between these pores and the zeolite crystals located in the particles. The complete model for this diffusion mode is provided. The model is confirmed by the experimental results. Diffusion also plays a very important role in many functions of biomembranes. A number of recent studies have revealed a complex structural organization of lipid bilayers. One of the most important features of the bilayer structure is the existence of cholesterol-rich microdomains, which are often referred to as lipid rafts. Lipid rafts are believed to play an important role in many functions of biomembranes, such as signal transduction. Therefore, studies of the influence of domains on the lipid self-diffusion are of significant interest. A meaningful study of this influence requires an ability of monitoring lipid diffusion in the broad range of displacements covering both the displacements, which are smaller and larger than the domain size. As a result the information on: (i) the diffusivities in and outside of domains, and (ii) the possible transport barriers on the domain margins can be directly obtained. First PFG NMR data along this direction will be presented and discussed.

**9:30 AM N8.3**
**Ballistic and diffusive random walks in confinement: About morphology, connectivity and reactivity in disordered porous systems.** Pierre Emile Levitz, Cecile Vigouroux and Dominique Petit; PMC, CNRS-Ecole Polytechnique, Palaiseau, France.

Gas diffusion inside disordered porous systems offers the possibility to study Pearson random walks. During this process, the trajectory of a diffusing particle is submitted at stochastic times to random reorientation of the velocity direction along random jumps exponentially distributed in length. These random walks are bounded by the pore network interface. The pressure modulation allows to change the particle mean free path and to move continuously from a ballistic regime (the so-called Knudsen regime at very large mean free path) to a molecular diffusion regime. General properties of such random walks in general bounded systems are not very well known. More especially, the roles of the pore morphology, the pore network topology and the surface reactivity in different diffusion regimes have to be clarified. At the practical point of view, the connection between the pore network architecture and the diffusive gas transport is a key point to monitor more cleverly the matrix formulation and to optimize transport in various diffusion regimes. In this presentation, a gas diffusion study has been undertaken in selected bimodal

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micro/macro porous materials widely used for gas separation. Either PFG-NMR of Xe at high pressure or more macroscopic experiments such as transient pressure techniques have been used in molecular and Knudsen regimes respectively. Extended morphological analysis has been conducted on random sections of these materials using scanning electron microscopy. These observations have permitted, using a constrained annealing algorithm, to build realistic 3D numerical models of these materials. In these reconstructed media, gas diffusion in molecular and/or Knudsen regimes were simulated and compared with success to experimental data. A topology analysis of these porous systems was performed using a new method to compute the line skeleton graph. This last part provides a way to analyze different contributions acting in these diffusive transport processes. This point is discussed and comparison with other recent works in this field is finally presented. Contact Email: levitz@pmc.polytechnique.fr.

## 10:15 AM *N8.4
### Self-Assemblies of Magnetic Colloids as a Tool to Confine Single Nanoscale Complexes.
Jerome Bibette, Laetitia Cohen-Tannoudji, Jean Baudry and Emanuel Bertrand; ESPCI, Paris, France.

This talk presents a new approach to study both the kinetic of bio-complexes formation and their mechanical properties (bending, stretching and compression). Self-assembling of magnetic colloids under magnetic field allows to impose colloidal distances and forces. Therefore the confinement and applied stress between grafted biomolecules can be monitored during contact duration. Moreover, the corresponding average time scale of the complex formation can be directly measured by counting the number of colloidal doublets that persist after the field is switched off. Once linked together magnetic particles transform into long magnetic filaments. From these structures, the bending rigidity of linkers as well as their force distance behavior, at a single link level is determined. Finally we present some dynamical properties of these artificial flexible filaments, and particularly their ability to swim and transport colloidal objects or cells.

## 10:45 AM N8.5
### Equilibrium Properties of Dilute Polymer Solution in Porous Media and Interaction Polymer Chromatography.
Yefim Brun, DuPont Central Research & Development, Wilmington, Delaware.

In recent years, interaction polymer chromatography (IPC) has become a popular technique for characterization of synthetic and natural polymers using separation of individual fractions by molecular properties other than size or molar mass of macromolecules. In IPC, as in any chromatographic technique, separation occurs due to thermodynamic partitioning between the sample components in the mobile and stationary phases. The partitioning takes place in a solution inside a chromatographic column packed with porous particles, and is caused by steric and adsorption interactions between macromolecules and the internal surface of the particles. This makes polymer adsorption a fundamental part of the separation process in IPC. The objective of this presentation is to demonstrate how the statistical theory of dilute polymer solution in confined (porous) media predicts and quantitatively describes different modes of chromatographic separation of complex polymers. One exciting example, which follows directly from the theory, is so-called critical point of adsorption (CPA), where repulsive polymer-surface steric (excluded volume) forces responsible for change of conformation entropy of a macromolecule, and short-range polymer-surface attractive forces with enthalpic nature, completely counterbalance each other. At such a point, in the limit of infinitely long macromolecules, first- or second-order phase transitions take place that lead to molar mass-independent elution of macromolecules experimentally observed for many polymeric systems. The existence and the order of such a threshold where all macromolecules simultaneously exist either inside or outside pores, depend on microstructure and topology of polymer chains, geometry of pores, etc. In theory, the fraction of adsorbed segments can be treated as the order parameter of the system and corresponding nonequilibrium free energy is calculated as a function of this parameter using different models of polymer chains. The existence of CPA and other fundamental properties of IPC following from the general principles of polymer adsorption, open opportunities for chromatographic fractionation of polymers by differences in chemical composition and microstructure of macromolecules. On the other hand, chromatographic behavior of polymers can serve as a direct experimental verification of the theory of polymer adsorption, including the effect of pore geometry, size and structure of macromolecules, and polymer-sorbent interaction energy on thermodynamic properties of the system. One important example will be considered in detail, i.e., how the theory of adsorption of heterochain macromolecules on heterogeneous surface explains the peculiarities of gradient separation of statistical copolymers by chemical composition and chain microstructure.

## 11:00 AM *N8.6
### Solvent behavior in hydrophobic silica nanotubes.
Douglas S. English[1], Sang Bok Lee[1], Karthik Jayaraman[1], Charles Luckett[1], Sang Jun Son[1] and Kenji Okamoto[2]; [1]Deptartment of Chemistry and Biochemistry, University of Maryland, College Park, College Park, Maryland; [2]Deptartment of Chemistry, Kyoto University, Kyoto, Japan.

Template-synthesized silica nanotubes offer a unique and interesting opportunity for studying fluids in confined spaces. Their versatility stems from our ability to independently vary the inside diameter and surface chemistry. In this work we investigate wetting strength and liquid phase stability for binary mixtures of water and methanol in hydrophobic nanotubes with internal diameters of either 30 or 170 nm. An improved sol-gel template synthesis process was used to prepare silica nanotubes with smooth and uniform walls within the pores of alumina template membranes. The pore diameter and thickness of the template membrane determine the tube outer diameter and length, respectively. The number of deposition cycles controls the wall thickness. Octadecylsilane coatings are applied selectively to the nanotube interior while leaving the nanotube exterior unmodified. Hydrophobic nanotubes are labeled with adsorbed dyes and the diffusion of the dye molecules inside individual nanotubes is investigated using fluorescence recovery after photobleaching (FRAP) experiments. Dye diffusion is used to monitor the wettability of the nanotube interior as a function of solvent composition and nanotube internal diameter. Our results show that wetting strength in the sub 200 nm regime is not inversely proportional to nanotube diameter as predicted from macroscopic theories of capillarity. Alternative theories to describe capillarity and wetting at the nanoscale are addressed.

## 11:30 AM N8.7
### Flow and Confinement Effects on the Evolution of Surfactant Mesophases.
Kareem Reda[1], Anubhav Tripathi[1], Jacinta Dossantos[2] and Arijit Bose[2]; [1]Division of Engineering, Brown University, Providence, Rhode Island; [2]Department of Chemical Engineering, University of Rhode Island, Kingston, Rhode Island.

A microfluidic platform is used to examine evolution of surfactant aggregate microstructures in highly constrained domains. Surface effects dominate because of the high area/volume ratio in these channels, and because of the proximity of boundaries, steric constraints and boundary chemistry impact both the range of available morphologies as well as the dynamics of aggregate formation. The small liquid volumes and precise metering, the ability to control domain dimensions that can vary from several orders of magnitude greater than the aggregate size to the order of the aggregate size, and in-line optical imaging and spectroscopy permits rapid evaluation of kinetics, morphology and phase behavior. The micelle-to-vesicle transition in aqueous solutions of sodium octyl sulfate (SOS) and cetyl trimethyl ammonium bromide (CTAB) are explored using a probe fluorophore to track microstructure changes and turbidity to monitor size changes. Our results will focus on the differences in aggregation and flow behavior between bulk and confined systems.

## 11:45 AM N8.8
### Mictrostructured Surfaces for Drag Reduction Purposes: Experiments and Simulations.
Hakan Rapp, Igor Zoric and Bengt Kasemo; Dept. of Applied Physics, Chalmers University of Technology, Goeteborg, Sweden.

It is well established that properly structured surface exhibits a lower friction drag, when exposed to a turbulent boundary layer, than a smooth surface under the same flow conditions. Examples of structures used for friction drag reduction include riblets, chevrons, etc, oriented in the streamwise direction. A drag reduction up to 10%, as compared to a smooth surface, was reported in the literature and usually attributed to an increased thickness of the viscous sublayer. In this work we address two related issues: i) how to optimize the geometry of the friction drag reducing structure and ii) provide an understanding of the friction drag reduction mechanism. Two approaches towards achieving above goals are presented. i) Fast, efficient, accurate and cheap methods, like photolithography and colloidal lithography were used to manufacture diverse surface structures (riblets, chevrons, etc), in the 1-50 $\mu$m range, on a standard 4$''$ silicon wafer. A special compact plane channel system was designed for measurements of the frictional drag on micrometer size structured surfaces in the turbulent flow covering a wide Reynolds number range. Because of the small size of the used drag reducing structures one can easily carry out measurements in the region of the turbulent flow where only drag reduction is taking place (no contribution from drag increasing effects). This region has not been accessible for experimental scrutiny so far. However, only the measurements of the drag reduction carried out in this region should be compared to the model calculations that attributes the drag reduction to an increased thickness of the viscous sublayer. ii)

Navier-Stokes equation, for the examined drag reducing geometry, was solved with appropriate boundary conditions. The resulting velocity field was used to extract the difference in the protrusion heights of the streamwise and spanwise flows over the structured surface. The latter was then related to the measured drag reduction slope. A comparison of the experimental results and simulation predictions, for structures containing rectangular micrometer sized riblets with varying height, spacing and thickness was carried out. We have shown that, in case when riblet structure is of the order of a wall unit, the observed drag reduction can be accounted for within the above model. Furthermore, by analyzing the measurements in the flow region when friction drag decrease and increase are present we show that for a rectangular ribbed surface the range of the drag reduction is determined primarily by the groove geometry rather than by riblet thickness and spacing. The magnitude of the maximum drag reduction is strongly dependent on the relative groove area. The maximum drag reduction for rectangular riblets occurs at $w^+=15$. This suggests that grooves rather than riblets are responsible for the shape of the drag reducing curves of ribbed surfaces.

SESSION N9
Chair: Alexander Neimark
Thursday Afternoon, December 1, 2005
Room 202 (Hynes)

**1:30 PM *N9.1**
**Synchrotron X-Ray Scattering Studies of the Surface Structure and Dynamics of Liquids and Liquid Films.**
Sunil Sinha[1,2], Hyunjung Kim[3], H. Lee[3], Y. Lee[3], Zhang Jiang[4], Laurence Lurio[5], Xuesong Jiao[5], Mirian Rafailovich[6], Chunhua Li[6]; [1]Physics, Univ. California San Diego, La Jolla, California; [2]LANSCE, Los Alamos Natl. Laboratory, Los Alamos, New Mexico; [3]Sogang University, Seoul, South Korea; [4]University of California, San Diego, La Jolla, CA; [5]North Illinois Univeristsy, De Kalb, IL; [6]SUNY-Stony Brook, Stony Brook, NY.

We shall briefly review the techniques of X-Ray reflectivity and off-specular diffuse scattering and the use of coherent X-ray beams and X-ray photon correlation spectroscopy to study the relaxation dynamics of capillary waves on polymer films as they approach the glass transition. We shall present recent results on the study of thin polystyrene films. These show strong interaction and confinement effects in their dynamics, which will be discussed. We shall also show how the technique may be used to generate information about the fluctuations at buried interfaces of bilayer films.

**2:00 PM N9.2**
**Effects of Composition and Stress Relaxation on the Glass Transition Temperature in Thin and Ultrathin Polymer Films: Intrinsic Fluorescence Studies of Polystyrene and Styrene-containing Copolymers.**
Manish Kumar Mundra[1] and John M. Torkelson[1,2]; [1]Materials Science Engineering, Northwestern University, Evanston, IL., Illinois; [2]Chemical and Biological Engineering, Northwestern University, Evanston, Illinois.

Nanoscale confinement can lead to significant deviations from bulk polymer behavior, including that related to glass transition temperature (Tg), physical aging, thermal expansion coefficient, etc. Several studies have suggested that the residual stresses built in during the spin coating process may be responsible for the some of the anomalous Tg behavior in thin and ultrathin films; however, relatively few studies have directly investigated the impact of residual stresses on Tg in confined geometries. In this study, we have employed intrinsic fluorescence as a versatile characterization tool for qualitatively measuring the residual stresses and quantitatively determining their impact on Tg in thin and ultrathin polystyrene (PS) and styrene-methyl methacrylate (S / MMA) random copolymer films. Intrinsic fluorescence of PS and other polymers is highly sensitive to local polymer conformational populations in solution and to local microenvironments in bulk homopolymers. This particular aspect of intrinsic fluorescence makes it ideal for studying relaxation of residual stresses in thin and ultrathin films. For films supported on quartz with naturally occurring surface hydroxyl units, Tg decreases dramatically with nanoconfinement for PS films. However, this effect may be tuned with increasing methyl methacrylate content in the copolymer. For instance, a 42 / 58 % S / MMA copolymer film of thickness 23-nm shows a decrease of 7 K in Tg relative to its bulk Tg value, whereas, a 22 / 78 % S / MMA copolymer film of similar thickness shows an increase of 8 K in Tg relative to its bulk Tg value. The effect of MMA content can be understood by the fact that MMA can have attractive interactions with the substrate (H-bonding), resulting in a less mobile layer right next to the substrate with higher Tg. Results for the thin and ultrathin films show that relaxation of the residual stresses can impact Tg substantially when measured during the first heating cycle as compared to when measured during the cooling cycle. Relaxation of the residual stresses during the heating cycle results in altering the local polymer conformational populations, in turn affecting the Tg values. On the other hand, during the cooling cycle from the rubbery state, no impact of residual stresses is observed because most of these stresses are relaxed even before the start of the measurement. Further, results indicate that the residual stresses built in during the spin coating process can lead to negative thermal expansion coefficient if not relaxed properly (for example during first heating cycle). Results also indicate that it is not sufficient to heat the polymer thin films just above its Tg to relieve these residual stresses but to values close to Tg + 20°C for roughly 20 min (or at yet higher temperature for shorter time) in order to relax these residual stresses completely.

**2:15 PM N9.3**
**Evidence for Glassy Dynamics and Re-Entrant Glass Transition in Laponite-Polymer Systems.**
Hossein Allen Baghdadi and Surita R. Bhatia; Chemical Engineering, University of Massachusetts - Amherst, Amherst, Massachusetts.

Laponite is a charged disk-shaped colloid that forms a glass under the appropriate conditions. The viscoelasticity of these systems shows rich kinetics, where the elastic modulus increases over time. The addition of low molecular weight poly(ethylene oxide) (PEO) induces a depletion force that melts the glass, reducing the viscosity and elastic modulus over all time scales. The addition of high molecular weight PEO forms a network, enhancing the elastic modulus of the system. At a critical molecular weight the absorbed polymer is able to bridge between laponite particles, reforming an elastic solid. We have studied the dynamics in these systems using both rheology and dynamic light scattering. The critical molecular weight of the polymer is shown to scale with the inter-particle spacing of laponite. The melting and reformation of glassy states has been seen in other colloidal systems by similar techniques.

**2:30 PM N9.4**
**Differences in the Effects of Nanoconfinement on the Distributions of Glass Transition Temperature and Physical Aging in Polymer Films: Novel Fluorescence Studies.**
Rodney D. Priestley[1], Manish K. Mundra[2], Perla Rittigstein[1], Linda J. Broadbelt[1] and John M. Torkelson[1,2]; [1]Chemical and Biological Engineering Dept., Northwestern University, Evanston, Illinois; [2]Materials Science and Engineering Dept., Northwestern University, Evanston, Illinois.

The fluorescence of dye-labeled poly(methyl methacrylate) (PMMA) films supported on quartz has yielded the distributions of glass transition temperature (Tg) and physical aging rates in nanoconfined polymers. Tg values are obtained by modeling the T-dependences of intensity as linear functions in the liquid and glassy states and assigning Tg to the intersection. Due to attractive H-bonding interactions at the PMMA-substrate interface, Tg increases with nanoconfinement. Tg distributions are obtained with multilayer films in which only one layer contains dye-labeled PMMA. At a thickness of 12-14 nm, the free-surface layer exhibits Tg - Tg,bulk = - 6 to - 8 K. A greater effect is found at the polymer-substrate interface. Using bilayer films with the substrate layer containing dye-labeled PMMA and an unlabeled bulk overlayer, the Tg value of the substrate layer increases with decreasing layer thickness below 60 nm. At 12-14 nm thickness, the substrate layer exhibits Tg - Tg,bulk = 9 to 10 K. For a film thick enough to exhibit bulk Tg values, trilayer studies show that a 12-nm-thick labeled layer exhibits a deviation from Tg,bulk when located 40 nm from the substrate interface and 20 nm from the free surface. Interesting nanoconfinement effects are observed when the multilayer thickness is below 100 nm. In bilayer films, a 12-nm-thick free surface layer exhibits an increase in Tg with decreasing bilayer film thickness, with Tg = Tg,bulk at an overall thickness of 80 to 100 nm and increasing to Tg,bulk 4 K at an overall thickness of 27 to 37 nm. In contrast, a 12-nm-thick substrate layer exhibits a reduction in Tg with decreasing bilayer thickness. When the bilayer thickness is 250 nm, the substrate layer exhibits Tg - Tg,bulk = 10 K; with a bilayer thickness of 37 nm, the substrate layer exhibits Tg - Tg,bulk = 4 K, identical to that of the free-surface layer in a 37 nm thick bilayer film. Thus, with nanoconfinement, the film does not support a substantial gradient in Tg values; when both free surface and attractive polymer-substrate effects are present in nanoconfined systems, the attractive polymer-substrate effect dominates, e.g., the free surface can exhibit a Tg value exceeding Tg,bulk. Both surfaces and polymer-substrate interfaces yield suppressed physical aging, with aging rate reduced from the bulk by a factor of 2 in a 25-nm-thick free surface layer sitting atop a bulk underlayer and by a factor of 15 in a 25-nm-thick substrate layer capped by a bulk overlayer. With trilayer films, the aging rate differs from bulk values in a 25-nm-thick layer located 100 nm from the free surface or the substrate interface. Studies on trilayer films indicate that Tg values are not impacted this far from the polymer-air or polymer-substrate interfaces. These dramatic differences indicate that there is much to characterize and to understand regarding the effect of confinement on glassy state dynamics.

**3:15 PM** <u>N9.5</u>
**Polymers in Random Nanoporous Glasses as Investigated by Dielectric, Thermal and Neutron Spectroscopy.**

<u>Andreas Schoenhals</u>[1], Christoph Schick[2], Bernhard Frick[3] and Reiner Zorn[4]; [1]Federal Institute for Materials Reserch and testing, Berlin, Germany; [2]Department of Physics, University Rostock, Rostock, Germany; [3]Institute Max von Laue - Paul Langevin, Grenoble, France; [4]Institute of Solid State Research, Juelich, Germany.

The features of glassy dynamics are distributed over a wide time and spatial scales and occur in a broad temperature range. The increase of the relaxation times with decreasing temperature over more than 14 decades close to the glass transition can be interpreted assuming a cooperative behavior which increases with decreasing temperature. The question is if there is experimental evidence for such a length scale. Its relevance can be indirectly proven by investigating molecules confined to hosts with restricting dimensions on the nanometer scale. The molecular dynamics of poly(propylene glycol) (PPG), poly(dimethyl siloxane) (PDMS) and poly(phenyl methyl siloxane) confined to nanoporous glasses (pore sizes: 2.5 .. 20 nm; native and silanized surfaces) revealed by broadband dielectric spectroscopy, temperature modulated DSC and neutron scattering are compared. The results reveal that the molecular dynamics of polymers in the pores is determined by a counterbalance of an adsorption and a confinement effect. The former slows down the molecular dynamics whereas the latter points to an inherent length scale responsible for glassy dynamics. The relevance of a characteristic length for glass transition is further supported by a change in the temperature dependence from a Vogel/Fulcher/Tammann behavior to an Arrhenius-like one found for the siloxane polymers as well as by the strong decrease of the step of the specific heat capacity with decreasing pores size at the glass transition.

**3:30 PM** <u>N9.6</u>
**Elasticity Measurement of Water Meniscus Using Small-Amplitude AFM.**

<u>Wonho Jhe</u>[1,2], Mun-Heon Hong[1], Hwansung Choe[1], Yongho Seo[1], K. Lee[2], G. Kim[2], Y. Cho[2] and J. Ihm[2]; [1]Center for Near-field Atom-photon Technology, Seoul National University, Seoul, South Korea; [2]School of Physics, Seoul National University, Seoul, South Korea.

We have employed a high-resolution non-contact atomic force microscope in air and achieved the spontaneous formation of a nanometric liquid column between a hydrophilic substrate surface and a Si cantilever tip. Also, we performed the sensitive measurement of the elastic property (or the force gradient) of the thin water column during its mechanical stretch through force gradient spectroscopy. A trident-type quartz crystal was employed as a force sensor and a commercial cantilever tip was attached at a prong of the quartz crystal sensor [1]. The resonance frequency of this quartz crystal is approximately 1 MHz. And the experiment was performed in amplitude detection mode using a radio frequency lock-in amplifier (SR844). The oscillation amplitude was about 0.1 nm and the frequency shift was estimated from the measured amplitude reduction based on a pre-measured frequency response spectrum of the tip-attached trident type quartz crystal force sensor. In contrast to a conventional micro-fabricated cantilever-based AFM used either in contact or noncontact operation mode, our AFM tip is stiff enough (k $\sim$ 105 N/m) to pull the condensed water molecules, as well as sensitive enough to measure the small changes of force gradient ($\sim$ 0.1 N/m). Figure (a) shows the measured force-gradient distance curve at a relative humidity of 2% and no hysteresis related to water meniscus was observed. The silicon cantilever tip and a freshly cleaved mica substrate were used. On the contrary, in figure (b) the force-gradient data was obtained at a relative humidity of 15% and a force-gradient hysteresis related to water meniscus formation was observed. Interestingly, step-wise force gradient change was observed when the hydrophilic tip was retracted after approaching the surface within a pre-defined distance. The work may give another application of noncontact atomic force microscope and provide a novel experimental tool for studying the kinematics of the condensed or adsorbed liquids on surfaces, which is of fundamental and technological interest in surface science and engineering. [1]Y. Seo, H. Choe, W. Jhe, Appl. Phys. Lett. 83, 1860 (2003)

**3:45 PM** <u>N9.7</u>
**Spontaneous Imbibition of Liquids into Nanopores.**

<u>Patrick Huber</u>, Department of Physics and Mechatronic Engineering, Saarland University, Saarbruecken, Germany.

It is of fundamental interest, whether macroscopically determined wetting properties or values of fluid parameters, such as the viscosity, $\eta$, or the surface tension, $\gamma$, accurately describe a liquid down to very small length scales, on the order of its building blocks. To address this question and some related aspects of flow in restricted geometries, we have investigated the spontaneous imbibition (capillary rise) of water, chain-like (linear and branched hydrocarbons), and rod-like molecules (liquid crystals) into nanoporous, monolithic silica glass as a function of temperature, T, and pore diameter, d (d=5-10nm). An analysis of the mass uptake of the porous monoliths versus time, m(t), allows us to determine a characteristic speed of the imbibition process, $v_{imb}$, which gives access to the fluid parameters of the confined liquid, $v_{imb} \sim \eta/\gamma$. For imbibing water, squalane as well as for the linear n-alkanes ($C_8H_{18}$-$C_{30}H_{62}$) we find no deviations of the fluid properties compared to the bulk ones. Within a model that describes the matrix as a bundle of independent parallel capillaries, the bulk values of $\eta$ and $\gamma$ account for our findings. By contrast, the flow of rod-like liquid crystals (e.g. 8OCB) is more sensitive to spatial confinement. Depending on shear rate and temperature, we observe different imbibition regimes, which are discussed in terms of geometric and shear alignment effects, viscous fingering instabilities as well as a no-slip/free-slip transition occurring at the walls of the nanopores. These aspects are further elucidated by x-ray diffraction experiments on the static structure factor of the liquids confined in well-aligned, tubular mesopores of silicon. Finally, we relate our results to the significantly changed crystallization behavior of hydrocarbon melts in nanopores, reported only recently (1). (1) P. Huber, D. Wallacher, J. Albers, K.Knorr, Europhysics Letters **65**, 351 (2004).

**4:00 PM** <u>N9.8</u>
**Qualitative Changes in Properties of Liquid Crystal Confined in Very Narrow Pores.**

<u>Manuel Rivera</u> and Fouad M. Aliev; Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

Dielectric spectroscopy, dynamic and static light scattering were used to investigate the influence of confinement of the liquid crystal 5CB (LC) on the nematic-to-isotropic (N-I) phase transition and the dynamics of molecular reorientations via rotation of molecules around their short axis under extremely narrow confinement in pores of 2.3 nm diameter, that may be considered a quasi-one-dimensional (1D) system. We did not observe the N-I transition in either dynamic and static light scattering experiments or dielectric spectroscopy experiments. We observed that, instead of undergoing the N-I phase transition, 5CB inside narrow pores solidifies: relaxation of molecular origin freezes out upon cooling the sample from the isotropic phase. Molecular reorientations were dielectrically active at temperatures above the bulk N-I transition temperature but with the relaxation rate much slower than that in the bulk. We observed that, instead of undergoing the N-I phase transition in the quasi-1D-system, 5CB inside the 2.3 nm pores solidifies. We suggest that the slowing down of the mode, which is molecular in the bulk material, is may be due to enhancement of the effective viscosity of 5CB under such narrow confinement and resulting glass-like dynamics.

**4:15 PM** <u>N9.9</u>
**Molecular motion in polymers at a shearing nanoasperity.**

<u>Greg Haugstad</u>[1], Andrew Avery[2], Craig Dystra[1] and Wayne Gladfelter[1]; [1]University of Minnesota, Minneapolis, Minnesota; [2]Unilever Research, Port Sunlight, United Kingdom.

New polymer technologies like nanoprobe read/write devices, as well as traditional technological arenas like lubrication and industrial processing, benefit from fundamental research on polymer-asperity interactions where nanoscale confinement plays a key role. We have investigated these interactions on several polymer thin-film systems with scanning probe microscopy. Here we focus on polydimethylsiloxane (PDMS) and polystyrene (PS) films, spanning a range of molecular weight. On PDMS films, for bulk liquid viscosities spanning several orders of magnitude, we find a transition from liquid-like to solid-like behavior below film thicknesses of approximately three times the radius of gyration. This is manifest as a decrease in sliding friction by two orders of magnitude, and concomitant disappearance of wicking behavior during probe retraction, below the transition thickness. We compare this finding with measurements under parallel-plate geometry by Yamada and coworkers (surface forces apparatus), where friction was observed to increase abruptly with decreasing film thickness, attributed to layering effects as chains are squeezed to integer multiples of chain diameter. The importance of interfacial topography, and its relevance to applications, is discussed. On PS films at room temperature (glassy in bulk), Fourier-analyzed nanoshear modulation measurements, together with post-measurement imaging, identify a time-evolving nonlinearity of shear interaction related to creep and plowing (dependent on entanglement). This behavior was unanticipated, and not generally observed, on glassy polymers. The implication of a highly mobile PS surface is discussed in conjunction with temperature and rate dependent sliding friction measurements by others, some of which suggested enhanced mobility relative to bulk. In contrast, our temperature and rate dependent characterization of the net displacement of PS during sliding (periodic bundle formation) reveals activation energies consistent with bulk values. We broaden the discussion of this conundrum to include our earlier findings on polymethyl methacrylate and (dry) gelatin films, as well as nanoscale

friction studies by other groups on PS and other polymers. The aggregate results on PS imply that early interpretations regarding intrinsic surface mobility were simplistic. We suggest that on some (and perhaps all) polymers, shear stress and energy transfer at a shearing nanoasperity modify conformational state population and rotational-isomer activation barriers. The nonlinear dynamical response of the interfacial nanosystem can differ markedly from the bulk intrinsic response.

**4:30 PM** <u>N9.10</u>
**Single Molecule Diffusion at Surface Steps.** Arne Schob and <u>Frank Cichos</u>; Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany.

The molecular interaction and dynamics at surface steps is a key issue for templating nanostructures by self-assembly at stepped surfaces. Such interactions play further a major role in fluidic applications. Micro- and nano-fluidics involve the flow of liquids in small volumes or channels, where the solid-liquid interface determines the transport properties of the whole liquid. Probing these interfacial properties is therefore a core ingredient for these types of applications including the general understanding of confined liquids. Within this presentation we describe for the first time measurements of the dynamics of single dye molecules in a liquid at stepped surfaces. Cleaved MICA provides large atomically flat surface regions with few straight steps on length scales of several micrometers and with heights of several hundred nanometers. Such surface steps offer an ideal tool to observe directly the interaction at the solid-liquid boundary by following the motion of molecules perpendicular to the step as well as parallel to the step surface. Our single molecule tracking experiments reveal a strongly anisotropic molecular mobility in the vicinity of the step, while it is completely isotropic on the smooth substrate. Molecules are trapped near the step for several ten microseconds, without being immobilized. The molecular mobility along the step is about two third of the mobility on the smooth substrate, while the diffusion constant perpendicular to the step is reduced by a factor of 5 compared to the smooth surface. The comparison of the measured anisotropy to an analytical model of the diffusion at a reflecting wall directly suggests a trapping potential depth of about 600 meV, which confines molecular motion to a region at the surface step. The high mobility along the step surface is explained by a rather weak trapping potential corrugation without specific adsorption sites. Further strong evidence for the importance of local surface ion distributions on the mobility of single molecules is provided.

**4:45 PM** <u>N9.11</u>
**Dielectric and Optical Properties of Polymer Confined in Random Porous Matrices.** <u>Fouad M. Aliev</u>, Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

We report the results of the investigations of the influence of confinement on the glass transition and dynamics of the alpha - and the beta-relaxation in poly(octylmethacrylate) (POMA) by dielectric spectroscopy. The polymer was synthesized and confined in pores of the random porous glasses with average pore sizes of 100nm and 10 nm. Both the alpha- and the beta- processes were observed in polymer confined to 100nm pores. The confinement is resulted in the reduction of the glass transition temperature Tg of the polymer mainly due to the existence of a developed pore wall-polymer interface and difference in the dynamic behavior of polymer in the surface layers compared to that in the bulk. The random structure of the host media was less important. The beta-processes in pores and in the bulk are similar at T<60C. In the vicinity of this T the beta-process, associated with the dynamical behavior of side groups, in confined polymer experiences strong changes in its temperature dependence. Light scattering experiments show an anomalous change in light scattering, which switches the composite from the opaque state to the transparent one, in a narrow temperature range around 60C. These changes could be explained by assuming that at low temperatures (opaque state) the orientational order of the relatively long linear aliphatic side groups is induced by the inner pore surface. For POMA confined in 10 nm pores we have not observed relaxation processes typical for bulk polymer.