SYMPOSIUM P

P: Dynamics in Small Confining Systems VII

December 1 - 4, 2003

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* Invited paper

SESSION P1:
Chair: Michael Urbakh
Monday Morning, December 1, 2003
Room 309 (Hynes)

8:30 AM *P1.1
Mechanical Properties of Atomic Sized Contacts. Ernst Meyer, Roland Bennewitz, Enrico Gnecco, Anisoara Socoliuc and Oliver Pfeiffer; Institute of Physics, University of Basel, Basel, BS, Switzerland.

Atomic-scale stick slip is investigated under ultrahigh vacuum conditions. Both the loading dependence and velocity dependence are studied with sharp probing tips on surfaces, such as KBr(001) and Cu(111). The velocity dependent atomic friction is discussed in terms of thermal activation. Microscopic parameters, such as the surface potential barrier height and the attempt frequency of this atomic sized contact, can be extracted out of these experiments. An increase of the loading can lead to a transition to the wear regime. Nanometer-scale modifications are produced and monitored by force microscopy. The fraction of energy is determined, which is used for friction and wear, respectively. First experiments to probe the mechanical properties of single molecules are presented.

9:00 AM *P1.2
Dynamics of Friction from Confined Films: Effects of Elasticity and Roughness. Mark O Robbins[1], Binquan Luan[1] and Gang He[2]; [1]Physics and Astronomy, Johns Hopkins Univ., Baltimore, Maryland; [2]Mechanical Engineering, MIT, Boston, Massachusetts.

The role of confined films in producing macroscopic friction has been the focus of great recent interest. Confinement can solidify films, which then transmit shear stresses between the confining solids. The yield stress of the film leads to static friction, and the stress required to maintain flow produces kinetic friction. Both stresses rise linearly with pressure, leading to macroscopic friction forces that obey Amonton's laws in most cases and explain prominent exceptions to these laws [1]. In the first part of the talk the velocity dependence of the kinetic friction is related to atomic dynamics and compared to recent work on rate dependent shear in bulk glasses. The second part of the talk considers the transition from smooth sliding to stick-slip motion as the sliding velocity decreases below a critical value v_c. A simple multi-scale approach is used to include the elasticity in the confining solids and v_c is evaluated as a function of the mass M, geometry and stiffness of the sliding body. The results resolve a controversy over the relationship between v_c and M. When the cross-section of the slider is independent of height above the contact, v_c becomes independent of M as M increases [2]. However, when the cross-section rises with distance from the contact, as in the Surface Force Apparatus, the slider is effectively rigid and v_c decreases as $M^{-1/2}$ as predicted by Robbins and Thompson [3]. The final part of the talk examines how surface roughness modifies the static and dynamic friction forces. 1. G. He, M. H. Müser and M. O. Robbins, Science **284** 1650 (1999). 2. B. N. J. Persson, Sliding Friction: Physical Principles and Applications (Springer, Berlin, 1998). 3. M. O. Robbins and P. A. Thompson, Science **253**, 916 (1991).

9:30 AM P1.3
Interaction Potential and Attempt Frequency in Nanoscopic Friction. Elisa Riedo[1,2], Enrico Gnecco[3], Roland Bennewitz[3], Ernst Meyer[3] and Harald Brune[1]; [1]Physics, EPFL, Lausanne, Switzerland; [2]Physics, Georgia Institute of Technology, Atlanta, Georgia; [3]Physics, University of Basel, Basel, Switzerland; [4]Condensed Matter Division, Institute of Physics, Basel, Switzerland.

The importance of thermally activated phenomena in nanoscopic sliding friction is highlighted by means of atomic force microscope (AFM) measurements of the velocity dependence of sliding friction [1,2]. These phenomena can be water capillary condensation in the interstitials between the sliding bodies [1] or tip hopping on the interaction potential [2]. Being related to the probability of transition between different equilibrium configurations, thermal activation is more efficient at low AFM tip velocities, i.e. for longer contact time there are higher probabilities to activate the process (condensation or hopping). When a nanometer sized tip slides on a surface, the atoms in contact have to overcome an energy barrier similar to atoms diffusing on a single crystal surface. Surprisingly, only few experimental studies have addressed the connection between friction forces and the atomic interaction potential. In our studies we relate nanoscopic sliding friction to the thermally activated hopping of the atoms forming the contact on an effective atomic interaction potential [2, 3]. We demonstrate that due to the thermally activated hopping of the AFM tip on a surface potential, the friction force increases logarithmically with the sliding velocity. The load dependence of the corrugation of the interaction potential and the hopping attempt frequency are determined for an AFM tip on a solid surface by means of a general analytical expression relating these quantities to the velocity dependence of the friction force. We find that the corrugation is roughly proportional to the applied load. The attempt frequency falls in the range of mechanical eigenfrequencies of the probing tip in contact with the surface. The picture of friction as a hopping mechanism is further confirmed by measurements of sliding friction while applying lateral nanometer oscillations to the cantilever at different frequencies. A surprising decrease of the friction force has been observed when the frequency of the oscillations is equal to the previous found attempt frequency. This finding open new possibilities to design low friction nanodevices. [1] E. Riedo, F. Levy, H. Brune, Phys. Rev. Lett. 88 (2002) 185505 [2] E. Gnecco, et al. Phys. Rev. Lett. 84 (2000) 1172 [3] E. Riedo, E. Gnecco, R. Bennewitz, E. Meyer, H. Brune, submitted to Phys. Rev. Lett.

10:15 AM *P1.4
Inter-Chain Interactions and Dynamics at Shearing Polymer Interfaces. Jacob Israelachvili, Matthew Tirrell, Nobuo Maeda and Nianhuan Chen; Chemical Engineering, University of California, Santa Barbara, California.

It is now well established, both experimentally and theoretically, that there is an intimate relationship between the two energy-dissipating processes of adhesion hysteresis and friction of moving surfaces. This relationship appears to be complex – involving both the physical and chemical properties of the surfaces, as well as the dynamics of processes themselves such as the sliding velocity or shear rates, the previous history, etc. In an attempt to identify the different roles of molecular- or nano-scale, micro-scale, and macro-scale processes we have studied the adhesion hysteresis and friction of various polymer surfaces under various conditions of molecular weight, glass transition temperature, density of surface loops and ends exposed at the surfaces, the lengths and geometry of the exposed end-groups, and the effects of adding polar groups to non-polar segments. Surface Forces Apparatus (SFA) experiments reveal that the last 1-2 nm of a surface has a profound effect on adhesion and friction, although the bulk substrate properties also play an important but different role in determining the overall energy-dissipating behavior of the whole system. Thus, the interdigitation of only a few segments across an interface can increase the adhesion hysteresis and friction forces by more than an order of magnitude, while bulk elastic and viscoelastic flow effects can determine such factors as the occurrence of stick-slip rather then smooth sliding. Other characterization techniques, such as neutron reflectivity, are also being used to gain better molecular-level insights. These observations suggest that many mechanical properties are critically dependent on the properties, both static and dynamic, of the first few layers of atoms, molecules or molecular groups at an adhesive junction or grain boundary in way that may also be controllable to achieve certain desired properties of a "bulk" material.

10:45 AM P1.5
Rheology and tribology of polymeric gels using the Surface Forces Apparatus (SFA). Suzanne Giasson[1], Damien Calvet[1] and Joyce Wong[2]; [1]Department of Chemistry, University of Montreal, Montreal, Quebec, Canada; [2]Department of Biomedical Engineering, Boston University, Boston, Massachusetts.

We present the dynamic properties, i.e. G/ and G//, of polymeric materials (transient and cross-linked network hydrogels). The different materials used are polyacrylamide (PAAm) and polyethylene oxide (C18-PEO). To measure dynamic properties, we used a modified Surface Forces Apparatus (SFA) using a sliding attachment allowing lateral sliding and normal force between two surfaces to be simultaneously measured. The results are compared with bulk rheology data obtained using an AR2000 rheometer (TA Instrument). In discussing the results, we will discuss advantages and limitations of the SFA for determination of rheological and tribological properties of polymeric complex systems. There are several reasons for using SFA as a rheometer. First, the effective interaction areas can be controlled through the separation distance between the surfaces and can be much smaller than the ones involved using classical rheometer, making possible local properties measurements. Secondly, the investigation of the transition between bulk and thin film rheology is possible. Finally, depending on the viscoelastic character of the material, the effect of pressure or normal forces on the dynamic properties can be measured. We find that for a certain range of film thicknesses, the moduli (G/ and G//) of elastic cross-linked hydrogels obtained from the SFA and classical rheometer techniques are similar. However, using SFA, we also show how the elastic modulus (G/) depends on the normal force applied to the hydrogel film. Moreover, under certain conditions, i.e. under high shear strains, we are able to probe the transition from rheology to tribology. For transient networks (viscoelastic hydrogels), our results also show good agreement between the two techniques for a gap thickness of ca 50 μm. The evolution of G/ and G// with pressure and film thickness will also be discussed.

11:00 AM P1.6
Oscillating Needle Rheology: A New Probe of Surface and Interfacial Compressional Viscosity. Luigi Cristofolini[1,2] and Marco P. Fontana[1,2]; [1]Physics, University of Parma, Parma, Italy; [2]Istituto Nazionale Fisica della Materia, INFM-UdR Parma, Parma, Italy.

In our program of studying glassy systems in confined geometries on the nanoscale, we have developed a new technique to measure surface compressional viscosities of Langmuir monolayers. Our technique, Oscillating Needle Rheology (ONR), is based on the optical detection of small oscillations of a magnetized needle stabilized at the air/water interface and excited by an applied oscillating magnetic field; it is a modification of the recently developed Interfacial Surface Stress Rheometer (ISR) by Brooks et al. [1], the main difference being that by ISR one probes the shear modulus and viscosity, while our ONR technique probes the compressional modulus and viscosity. The range of compressional viscosities accessible by ONR is much larger than that accessible by the all-optical technique of Surface Quasielastic Light Scattering (SQELS), which also probes the complex compressional modulus, thus offering a complementary point of view on many systems, such as polymeric Langmuir monolayers, whose compressional modulus as a function of surface density spans over many orders of magnitude [2]. We shall describe applications of the technique to two selected systems stabilized at the air-water interface, namely polymeric azobenzene layers whose hydrophilicity can be controlled by the UV illumination [3], and phospholipidic monolayers whose mechanical properties are supposed to be modified by the adsorption of specifics proteins from the subphase, a process which may model the protein biological functionality in actual biomembranes [4]. [1] Brooks C. F., Fuller G. C., Frank C. W., Robertson C. R., Langmuir 15, 2450, 1999 [2] Cristofolini L., Cicuta P., Fontana M.P., J. Phys. Cond. Matt 15 S1031, 2003 [3] Cristofolini L., Fontana M.P., Berzina T., Konovalov O., Phys. Rev. E66, 041801, 2002 [4] Polverini E., Arisi S., Cavatorta P., Berzina T., Cristofolini L., Fasano A., Riccio P., Fontana M.P. Langmuir, 19 (2003)

11:15 AM *P1.7
Control of Friction at the Atomic Scale. Yehuda Braiman, Sangmin Jeon, Jacob Barhen, Vladimir Protopopescu and Thomas Thundat; Oak Ridge National Laboratory, Oak Ridge, Tennessee.

We will discuss techniques to control friction at the atomic scale, during sliding. Our experiments involve an AFM tip sliding on a vibrating surface mounted on a piezo-element. Theoretical/numerical results are focused on development of efficient algorithms to control friction towards targeted behaviors. In particular, we will discuss a terminal attractor algorithm to control frictional dynamics of an array of particles towards pre-assigned values of the frictional force. This control technique is robust and significantly reduces the transient time to reach the prescribed behavior. Moreover, only the average sliding velocity of the array is needed in order to apply the proposed control. This research was sponsored by the Division of Materials Sciences and Engineering, U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

11:45 AM P1.8
Comparison of FFM and SFA Friction Measurements on Aromatic Monolayers. M. Ruths, Dept. of Physical Chemistry, Åbo Akademi University, Åbo, Finland.

Friction force microscopy (FFM) and the surface forces apparatus technique (SFA) were used to study the boundary friction of self-assembled aromatic thiol and silane monolayers. The strength of the adhesion was varied by working both at dry conditions and with the surfaces immersed in a solvent. Under conditions of low adhesion, the dependence of the friction force on the contact area was significantly reduced, and good agreement was found between friction coefficients measured with the two techniques despite the large differences in the contact areas, forces and pressures. The friction forces were generally found to be lower when both sliding surfaces were covered with a monolayer, and plateaus in the friction force as a function of velocity found in the FFM experiments appeared at higher velocity, suggesting a more fluid-like sliding. The influence of contact area on the characteristics and magnitude of the friction force in adhesive systems is discussed.

SESSION P2:
Chair: Kathryn Wahl
Monday Afternoon, December 1, 2003
Room 309 (Hynes)

1:30 PM *P2.1
Creeping Friction Dynamics and Molecular Dissipation Mechanisms on Unstructured Polymer Surfaces.
Rene M. Overney and Scott Sills; Chemical Engineering, University of Washington, Seattle, Washington.

The dissipation mechanism of nanoscale kinetic friction, as function of temperature and scan velocity, between an atomic force microscopy (AFM) tip and a surface of amorphous polystyrene (below, around and above the glass transition) will be presented. Superposition of the friction results using the method of reduced variables revealed the dissipative behavior for both, the glassy state and the viscous rubbery state of the polymer, as an activated relaxation process with a potential barrier height of 7.2 kcal/mol for the glassy state, corresponding to the hindered rotation of phenyl groups around the C-C bond with the backbone. The velocity relationship with friction, F(v), was found to satisfy simple fluctuation surface potential models with F$\propto$const-ln(v) and F$\propto$const-ln(v)$^{2/3}$, which were developed for friction on periodically corrugated surfaces. Friction, within 10 K above the glass transition temperature, exhibited a van der Waals loop-like behavior that originates from flow hindrances such as cross-linking.

2:00 PM *P2.2
Sliding-Induced Non-Equilbibrium in Confined Systems.
Martin H. Muser, Department of Applied Mathematics, University of Western Ontario, London, Ontario, Canada.

When two solid walls are in relative sliding motion, the intervening layers separating the two walls is typically far from thermal equilibrium. The subsequent break-down of linear response makes a quantitative description of triobological contacts difficult. I will discuss the effects of far-from-equilibrium for two different models. One system consists of a simple boundary lubricant. Computer simulations reveal that the libricant's velocity distribution cannot be described as the sum over a few Gaussians. A central Maxwell-Boltzmann peak (related to thermal equilibrium) occurs plus non-Gaussian tails at large velocities. These tails barely change the average kinetic energy. However, they tremendously increase the probability of rare events, such as chemical reactions. Hence an effective chemical temperature would be much larger than an effective phonon temperature. This renders the concept of a (unique) non-equilibrium temperature ill-defined. [M. Aichele and M. H. Müser, Phys. Rev. E, submitted]. The second model mimics the sliding motion of polymer brushes in good solvents. We were particularly interested in identifying mechanisms that lead to enhanced dissipation under oscillatory shear in such systems when the driving amplitude reaches certain 'resonance' values. Two explanations were given for this phenomenon: One proposes a coincidence of intrinsic relaxation times and (inverse) excitation frequencies. The other explanation relates the enhanced dissipatin to stick-slip motion in the relevant regime. While both scenarios are legitimat, we observe yet another one. When the sliding direction is reversed, the end-grafted polymers are strongly compressed and the opposing brushes overlap significantly during certain stages of the itinerant reversal phase. The deformation of the polymers, whose configurations are far from stead-state sliding and thermal equilibrium, requires large amount of (free) energy, which ultimately will be dissipated as heat. [T. Kreer, K. Binder, and M. H. Müser, Langmuir, submitted].

2:30 PM P2.3
Hydrocarbon Boundary Lubrication with/without Nano-Particles. Manfred P. Heuberger[1], Jelena Manojlovic[1] and Carlos Drummond[2]; [1]Department of Materials, Swiss Federal Institut of Technology (ETH), Zuerich, Zuerich, Switzerland; [2]Centre de Recherche Paul Pascal, CNRS, Pessac, Bordeaux, France.

We confined thin films of the linear hydrocarbon hexadecane (C16H34) between mica substrates using two different variants of the surface forces apparatus (SFA). The response to reciprocating shear was measured. A comparative study using two different kinds of mica substrates is presented: Type A mica was prepared using the conventional melt-cut (hot Pt-wire), which was recently found to generate Pt nano-particles on the mica surface (1,2). Alternatively, we prepared type B mica by cutting the sample edges with surgical scissors to avoid generation of Pt nano-particles. Type A mica is found to quantitatively reproduce earlier results obtained in the SFA, including intermittent friction (stick-slip) and the existence of a critical velocity. In contrast, hydrocarbon films between Type B mica tend to be thicker for comparable external loads and the measured sliding is always smooth (i.e. no stick-slip) over all measured velocities and loads. The absence of intermittent friction indicates that the confined film does, in fact, not completely solidify as previously suggested. A unifying picture is discussed that accounts for the differences seen between type A and type B substrates, while including the known dependence of stick-slip to molecular details. (1) Ohnishi, S.; Hato, M.; Tamada, T.; Christenson, H. K. Langmuir 1999, 15, 3312-3316. (2) Kohonen, M. M.; Meldrum, F. C.; Christenson, H. K. Langmuir 2003, 19, 975-976.

3:15 PM *P2.4
Confinement effects and Friction at both Simple Fluid Solid and Elastomer Solid Interfaces. Liliane Leger, Hubert Hervet, Tatiana Schmatko and Lionel Bureau; Physique des Fluides Organises, College de France, Paris, France.

We shall present series of experiments developed on model systems in order to identify friction mechanisms at fluid solid and soft solid solid interfaces. For simple fluids, Near Field Laser Velocimetry (NFLV), has allowed to establish that, contrary to what is usually assumed in hydrodynamics, a simple fluid can develop noticeable slip at the wall on smooth surfaces, even in total wetting conditions. Examples will be given to illustrate how both the strength of the fluid solid interactions and the surface roughness, at nanometric scales, are key parameters governing the slip length. For polymer systems, both entangled polymer melts and crosslinked elastomers interfaces with solid surfaces covered by end grafted polymer chains have been investigated. Based on NFLV and direct friction force measurements, we shall show how the degree of confinement of the surface anchored polymer chains governs their aptitude in promoting interfacial friction. Systematic experiments based on polydimethylsiloxane (PDMS) entangled melts or crosslinked PDMS elastomers put into contact with smooth silica surfaces covered with grafted layers of PDMS chains with well defined molecular weights and surface densities will be presented. The results will be compared to recent models, and the molecular mechanisms of polymer polymer friction, for that particular situation where surface chains are fluid like and highly confined due to both grafting and shear stress will be clarified.

3:45 PM P2.5
Hydrodynamic Slip at Solid Surfaces: When Roughness Reduces Friction. Cecile Cottin-Bizonne, Lyderic Bocquet, Jean-Louis Barrat and Elizabeth Charlaix; Laboratoire PMCN, Universite Lyon I, Villeurbanne, France.

With the recent important development of microfluidic systems, miniaturization of flow devices has become a real challenge. Microchannels, however, are characterized by a large surface to volume ratio, so that surface properties strongly affect flow resistance in submicrometric devices. The dynamics of the fluid close to the solid surface now become a crucial ingredient to control. In hydrodynamics, the dynamics of the fluid at the wall is characterized by a boundary condition (BC) which is generaly assumed to be a no-slip BC : the velocity of the fluid is vanishing at the wall. If this condition is expected to hold at the macroscopic scale, this is not necessary the case at smaller length scales and one has to introduce the notion of fluid slip at the solid boundary. The corresponding BC is characterized phenomenologically by a extrapolation length, usually denoted as "slip length". However, there is a strong debate in the litterature about the value of this slip lentgh. The results found by different experimental groups, using various techniques, from FRAP to Surface Force Apparatus, via laser velocimetry, vary over a few orders of magnitude, from the ansgtrom to the micron (even for similar materials) ! If for some results a misleading data analysis may be invoked, some discrepancies cannot be solved. In this context, we present both theoretical and simulation results showing that the concerted effect of wetting properties and surface roughness may considerably reduce friction of the fluid past the boundaries. In particular we show that the slippage of the fluid at the channel boundaries is shown to be drastically increased by using patterned surfaces. This effect occurs in the regime where the surface pattern is partially dewetted, in the spirit of the 'superhydrophobic' effects that have been recently discovered at the macroscopic scales. Our results show for the first time that, in contrast to the common belief, surface friction may be reduced by surface roughness. They also open the possibility of a controlled realization of the 'nanobubbles' that have long been suspected to play a role in interfacial slippage. references : Quere D., Fakir Droplets, Nature Materials vol 1, 14-15 (2002). Tyrell J.W.G., Attard P, Images of nanobubbles on hydrophobic surfaces and their interactions, Phys. Rev. Lett., vol 87, 176104 (2001). Vinogradova O.L. et al., Submicrocavity structure of water between hydrophobic and hydrophilic walls as revealed by optical cavitation, J. Colloid Interface Sci. vol 173, 443-447 (1995). Jean-Louis Barrat, Lyderic Bocquet, "Large slip effect at a nonwetting fluid-solid interface", Phys. Rev. Lett. vol 82, 4671–4674 (1999). Cecile Cottin-Bizonne, Jean-Louis Barrat, Lyderic Bocquet, Elisabeth Charlaix, "Low friction liquid flows at nanopatterned interfaces", Nature Materials vol 2, 238-241 (2003).

4:00 PM P2.6
Nanofluidics: Viscous Dissipation in Layered Liquid Films. Frieder Mugele and Thomas Becker; Applied Physics, University of Ulm, Ulm, Germany.

We studied the layer-by-layer collapse of molecularly thin films of a model lubricant confined between two atomically smooth substrates. The dynamics of the consecutive expulsion of four molecular layers were found to slow down with decreasing film thickness but showed no evidence for confinement-induced solidification. Using a new hydrodynamic model, we show that the sliding friction of liquid layers on top the solid substrates is 18 times higher than the mutual friction between adjacent liquid layers. The latter was independent of film thickness and in close agreement with the bulk viscosity.

4:15 PM *P2.7
Intrinsic Friction of Monolayers at Solid Surfaces. Gleb Oshanin, Theoretical Physics of Liquids, University of Paris 6, Paris, France.

In this talk we overview recent results on the intrinsic frictional properties of adsorbed monolayers, either exposed to the vapor phase and undergoing continuous particles exchanges with it, or sandwiched between two solid surfaces. Within the framework of a dynamical Master equation approach, we determine the terminal velocity of some biased impure molecule - the tracer particle, constrained to move inside the adsorbed monolayer probing its frictional properties. As well, we define the nature of the effective frictional forces exerted on the tracer particle by the monolayer, obtain the force/velocity relation and discuss the form of the density profiles around steadily moving tracer which show, in some instances, remarkable power-law long-distance tails revealing thus an emergence of essentially cooperative behavior.

4:45 PM P2.8
Quasistatic Nanomachines. Valentin Popov, Institute of Mechanics, Technical University Berlin, Berlin, Germany.

The motion of systems of several bodies connected by bonds of varying lengths in a spatial periodic potential is examined. It is shown that the translational motion of such systems can be induced if system parameters (e.g., bond lengths) are changed in parameter space along closed paths containing singular points of the system. This mechanism of inducing the translational motion can be realized by application of a variable elliptically polarized electric field to nano-sized particles located on a chemically inert crystalline surface (e.g., graphite surface). The velocity of the particle motion can be controlled by the frequency of the electric field and its direction by the direction of elliptical polarization.

SESSION P3:
Chair: John Fourkas
Tuesday Morning, December 2, 2003
Room 309 (Hynes)

8:30 AM *P3.1
Living Bacteria Confined in Porous Silica. Jacques Livage[1], N. Nassif[1], C. Roux[1], T. Coradin[1], O. Bouvet[2] and M. N. Rager[3]; [1]Chimie Matiere Condensee, University Paris 6, Paris, France; [2]Unite INSERM, Chatenay Malabry, France; [3]Service de RMN, ENSCP, Paris, France.

The chemical conditions involved in the formation of silica via the so-called sol-gel process are mild enough for proteins to be encapsulated within the porous silica network. Small molecules can diffuse through the pores allowing biochemical reactions to be performed in-situ, within the sol-gel glass. A large number of enzymes have already been studied. They appear to be physically trapped and retain most of their biocatalytic properties. Recent experiments show that micro-organisms such as bacteria can also be trapped in silica gels. The enzymatic activity exhibited by *Escherichiacoli* is preserved inside the silica gel. It is even better than for free bacteria suspended in an aqueous solution. This was due to some lysis of the cell membrane during the encapsulation process. Bacteria actually behave as a "bag of enzymes", their cytoplasm remains trapped within the nanopores and lysis favours the diffusion of reactants through the membrane. The problem of the viability of bacteria in silica nanopores will then be addressed. Viable bacteria in which membrane integrity is preserved were evidenced by their metabolic activity and ability to form colonies. An aqueous route was developed in which the silica matrix appears to prevent the lysis of cell membranes and increase their viability. Confinement appears to be a major parameter as it prevents chemical communication between trapped bacteria and avoids the formation of colonies.

9:00 AM *P3.2
Exploiting Proteins in Restricted Spaces: Toward Tracheal Wound Restitution. Frank V Bright, Chemistry, University at Buffalo, The State University of New York, Buffalo, New York.

Questions regarding the behavior of protein activity, conformation, and stability within restricted environments impact numerous fields.

For example, protein behavior in restricted domains, relative to its native behavior, is crucial for the effective development of biosensors and tailored biomaterials for the controlled release of biologically active peptides and proteins. Examples of the latter include tailored biomaterials that release small peptides that exhibit candidacidal activity or the release of active cytokines and growth factors that can be used to promote reepithelialization. This presentation will focus on: [1] what motivates our efforts to study proteins in restricted microenvironments; [2] what are some of the key questions we seek to answer; and [3] how we exploit information on protein behavior in restricted environments actually develop better biomaterials.

9:30 AM P3.3
The dynamics of DNA-obstacle collisions. Greg C. Randall and Patrick S. Doyle; Chemical Engineering, MIT, Cambridge, Massachusetts.

We present a comprehensive study of single DNA molecules in electrophoretic motion colliding with a single microfabricated obstacle. During a collision, DNA impacts an obstacle and deforms; the impact conditions dictate whether this collision results in a "roll-off" event or "hooking" event. In this investigation, we postulate physical models that describe the full "phase-diagram" of collision events, which range from glancing "roll-off" collisions to symmetric hairpin "hooking" collisions. These models are supported by single molecule fluorescence microscopy experimental data. With fluorescence microscopy techniques, we can experimentally track the time evolution of the molecule's position and size during a collision event. In support of this work, these same experimental techniques are also used to study of the dynamics of single DNA molecules in confined environments. Analogous to simulation work by Jendrejack et al., we determine molecular diffusivity and relaxation time of single DNA molecules in various states of confinement. The models and data supplement work to create an improved DNA separation device for large DNA molecules (> 48.5 kbp) in which the separation mechanism is the collision of the DNA with a stationary obstacle.

10:15 AM *P3.4
Dynamics of Intrinsically Curved DNA and Random RNA Sequences Through Gels. Udayan Mohanty and Alexander Spasic; Chemistry, Boston College, Newton, Massachusetts.

We have explicitly solved the long standing problem of a quantitative predictive model that describes the electrophoretic mobility patterns of circularly-permuted oligomeric DNA molecules, all having the same length but with the bend positioned differently in each, in polyacrylamide gel of various concentration. The bends are due to short stretches of adenines (A-tracts) which were repeated in phase with the helical repeat. The model takes into account in an approximate way polyelectrolyte effects such as condensed and screened counterions, coulombic end effects, salt concentration, pH of the buffer, screening of the hydrodynamic interactions, flexibility of the molecule, concentration of the gel, as well as the characteristics of the interactions of the gel with the curved DNA. The predictions are in excellent agreement with the experimental data of Crothers and coworkers and of Thompson and Landy. A generalized of our model leads to a description of (i) the dynamics of phased A-tracts, where the A-tracts containing sequences are located at different phasing with respect to a bend of known magnitude, and (ii) the conformational order of small evolved and random RNA sequences. Specifically, we can describe the compactness of small evolved and random RNA sequences in the presence of varying concentration of magnesium from gel electrophoretic data. The results are compared with those obtained from sedimentation coefficient data of Schultes and Bartel.

10:45 AM P3.5
Enhanced diffusion of fluorescent probes in a hexagonal phase of cylindrical micelles. Yann Gambin[1], Wladimir Urbach[1], Gladys Massiera[2], Christian Ligoure[2] and Laurence Ramos[2]; [1]Laboratoire de physique statistique, Ecole Normale Superieure, PARIS, France; [2]Groupe de Dynamique des Phases Condensees, universite Montpellier 2, Montpellier, France.

We have studied diffusion anisotropy of a fluorescent probe in an hexagonal phase of cylinders, made of an oil core stabilised by a surfactant (SDS). In our experiments, the separation between cylinders is fixed (2.2 nm) whereas the radius is adjustable between 1.5 and 15 nm. The hexagonal phase is oriented by slow aspiration in glass microchannels. A fringe pattern photobleaching (FRAPP) under the microscope allows to measure precisely the diffusion of a fluorescent probe, a fluorescein group connected to an hydrophobic tail (CnH2n; n = 12, 16 or 18). The fringe orientation can be continuously varied allowing self-diffusion anisotropy measurements. Along the cylinders, the pattern relaxation of FRAPP exhibits a single exponential decay. The probe undergoes a characteristic brownian motion. The diffused distance x grows as the square root of time : $x \sim t\hat{1}/\mu$, μ=2, for interfringe values ranging from 10 μm to 150 μm. In the direction perpendicular to the main cylindrical axis of the micelles, we observed anomalous, enhanced diffusion : the apparent mobility increases with the interfringe : $x \sim t\hat{1}/\mu$, with μ ranging from 1.5 to 1.7 ($\pm$0.1). The characteristic diffusion time depends on the number of cylinders in a given interfringe i, and not on the cylinders radius, R. The measured diffusion times for i = 1.5 μm with R = 1.5 nm cylinders and for i = 15 μm with R = 15 nm cylinders are equal. The perpendicular diffusion constant is about three orders of magnitude slower than the diffusion along the cylinders and strongly depends on the length (n) of the hydrophobic tail of the probe. The smallest (n = 12) diffuses twice faster than the more hydrophobic one (n=18). The anomalous diffusion can be described by a Levy walks model that takes into account the time intervals spend by the walker between two steps. The extreme event, which can appear within a given number of steps covered, is a very short trapping time.

11:00 AM *P3.6
Intracellular Dynamics: Molecular Delivery along Microtubules. Michael Elbaum[1], Hanna Salman[1], Asmahan Abu-Arish[1], Shachar Oliel[2], Abraham Loyter[2], Joseph Klafter[3] and Rony Granek[4]; [1]Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel; [2]Alexander Silberman Institute of Life Sciences, Hebrew University of Jerusalem, Jerusalem, Israel; [3]School of Chemistry, Tel Aviv University, Ramat Aviv, Israel; [4]Department of Biotechnology Engineering and The Institute for Applied Biosciences, Ben Gurion University of the Negev, Beer Sheva, Israel.

Transport of macromolecules within the living cell is essential to its coordinated operation. One of the most important transport systems in higher organisms is that which guards access to the nucleus. Proteins are always expressed outside the nucleus, and may be imported to the nucleus according to the presence of short peptides, or signals, encoded within their sequence. These interact with a set of specific proteins acting as transport receptors, which mediate the translocation across the nuclear pores and delivery to the other side. The cytoplasm is a crowded environment, with many filamentous and membranous barriers to simple diffusion. At the same time the cytoskeleton provides networks of filaments along which cargos may be delivered by motor proteins. The microtubule network normally radiates from a point near the nucleus, offering a directed inward or outward path. Motor proteins of two families, kinesin and dynein, move along the structurally polarized microtubules. Most kinesins move in a direction corresponding to outward movement, while dynein moves inward toward the cell center, i.e. toward the nucleus. Movement of small vesicles along microtubules is visible in the light microscope. We have studied the interaction between these two transport systems, testing the hypothesis that proteins destined for entry to the nucleus may be delivered along microtubules. Using an extract of Xenopus frog eggs we could reconstitute in vitro both nuclei and randomly-oriented microtubule networks. We then prepared, as transport markers, large protein-DNA complexes carrying nuclear localization signals. Particle tracking and statistical analysis of their movement reveal an active drive, while chemical inhibitors show that it depends on microtubules and on dynein. A random velocity field model describes the directed path along such a random network. In the intact cell the same interactions would lead to nuclear delivery of protein substrates carrying nuclear localization signals.

11:30 AM *P3.7
Low Frequency Dynamics of Proteins in Confinement. Jean-Pierre Korb[1] and Robert Bryant[2]; [1]Laboratoire PMC, CNRS, Palaiseau, France; [2]Dept of Chemistry, University of Virginia, Charlottesville, Virginia.

The dynamics of a folded protein are complex and characterization requires examination over many decades in frequency or time. The magnetic field dependence of nuclear spin-lattice relaxation or the magnetic relaxation dispersion provides a powerful means for probing the fluctuation spectrum form the range of milliseconds to picoseconds. We report here magnetic relaxation dispersion measurements on proteins that have been rotationally immobilized to suppress the rotational averaging of proton-proton dipole-dipole couplings. One price of immobilization is loss of high resolution usually associated with proton NMR spectroscopy; however, the experiment provides a valuable characterization of the intramolecular protein dynamics at frequencies well below the rotational frequency of the protein in solution. The magnetic field dependence of the hydrogen nuclear spin-lattice relaxation rate constant reports the low frequency structural fluctuations along the protein backbone. The relaxation efficiency varies according to a power law at low magnetic field strengths, corresponding to low Larmor frequencies. The power law parameters may be related to the dynamical distribution of states, the localization of the disturbances, and the spatial distribution of hydrogen in the folded structure. We propose a theory that depends on the structural disturbances propagating along the polypeptide chain, which effectively reduces the dimensionality of the relaxation process. This process accounts quantitatively for the

experiment and may be loosely characterized as a localized direct spin-phonon coupling. This class of experiment provides a powerful approach to characterizing intra and intermolecular dynamics in proteins and other chain polymers.

SESSION P4:
Chair: Pierre Levitz
Tuesday Afternoon, December 2, 2003
Room 309 (Hynes)

1:30 PM *P4.1
Magnetically Modulated Optical Nano-Explorers for Imaging the Chemical and Physical Nano-Dynamics Inside Live Cells. Raoul Kopelman, Jeffrey Anker, Caleb Behrend and Brandon McNaughton; Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

Magnetically Modulated Optical Nanoprobes (MagMOONs) are novel nano-devices for biomedical applications. 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 to background ratio over existing techniques. The very simple micro/nano-fabrication techniques combine elementary chemistry and physics procedures.

2:00 PM *P4.2
Topology Matters: Some Aspects of DNA Physics.
Ralf Metzler[1], Andreas Hanke[2], Mehran Kardar[3], Yacov Kantor[4] and Paul Gunnar Dommersnes[5]; [1]NORDITA, Copenhagen OE, Denmark; [2]Inst. f. Theoretical Physics, Stuttgart University, Stuttgart, Denmark; [3]Physics Dept, MIT, Cambridge, Massachusetts; [4]Physics, Tel Aviv University, Tel Aviv, Israel; [5]Institut Curie, Paris, France.

Double-stranded DNA is one of the best known realisations of a self-avoiding polymer due to its small ratio between effective diameter and persistence length; moreover, it can be perfectly copied. Thus, DNA is of high interest to polymer physics, in particular, given the possibility of performing single molecule experiments on DNA strands. However, due to its heterogeneous character and the specific binding strengths ('kT-physics'), as well as its interaction with certain enzymes occurring in its natural biochemical environment, this biological macromolecule instigates the investigation of additional properties of (bio)polymers: (1) DNA knots and other entangled states: The enzyme topoisomerase II is able to detect knotted states in DNA and to actively reduce the degree of knottedness under consumption of ATP-energy. Given its necessarily local probing, how can the enzyme be so efficient in reducing the knottedness? It will be shown that tightening of the knot due to thermal fluctuations may facilitate this detection. (2) Single-stranded bubbles in double-stranded DNA: Already at physiological temperatures, short stretches of DNA open up due to fluctuations, to form flexible single-stranded loops ('DNA breathing'). Upon heating, the typical size of these fluctuation bubbles increases, until at the melting temperature, the two strands seperate fully. Recent single molecule experiments reveal the processive character of the breathing dynamics. A simple phenomenological model based on statistical mechanical properties of the DNA will be introduced to explain the details of the bubble dynamics. An analysis similar to the investigation of DNA knots allows modifications of the traditional DNA-melting models to explain the sharp melting transition of double-stranded DNA.
References: [1] M. D. Frank-Kamenetskii, Phys. Rep. **288**, 13 (1997). [2] R. Metzler et al., Phys. Rev. Lett. **88** 188101 (2002). [3] A. Hanke and R. Metzler, Phys. Rev. Lett. **90**, 159801 (2003). [4] A. Hanke and R. Metzler, eprint cond-mat/0305049. [5] A. Hanke and R. Metzler, Biophys. J. (in press), eprint cond-mat/0211468

2:30 PM P4.3
Tapping-mode AFM - Force Measurement Capabilities on Biomaterial Surfaces. Ijeoma Nnebe and James W Schneider; Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

The efficacy of biosensors and other functionalized biomaterials is largely dependent on the elimination of non-specific binding to the biomaterial surface. This is commonly achieved through the deliberate incorporation of hydrophilic polymer chains onto these surfaces as bulk antifouling layers. Polymers are also utilized to tether the active biorecognition element (receptor or ligand) allowing for greater motional freedom and an increase in the binding kinetics. In the design of these materials, it is therefore important to understand how the introduced polymer chains impact both the specific and non-specific interactions. Commonly, receptor-ligand binding strengths are measured using DC AFM with sharp tips to enhance lateral resolution. Often, the compression pressures associated with sharp tips result in indentation of soft adsorbed layers before measurable cantilever deflection. Additionally, the loads applied during this prolonged contact with the sample can be large enough to denature biomolecules. As an alternative, we use tapping-mode (TM) AFM with the aim of better preserving biological activity and to increase the sensitivity of measurement. Due to the large oscillation amplitudes used in this mode, binding can be achieved with minimized contact time and load. We model the cantilever dynamics as a modified forced damped harmonic oscillator and have successfully modeled TM force curves on a variety of surfaces after accounting for distance-dependent energy dissipation in the system. This energy dissipation is characterized for each particular force measurement using the resonance behavior of the cantilever. We have validated the technique through the independent measurement of poly(ethylene glycol), PEG, steric forces and streptavidin-biotin interactions on homogeneous surfaces and we further extend the technique toward the simultaneous measurement of these interactions on heterogeneous surfaces.

3:15 PM *P4.4
The Fluctuating Enzymes. Sunney Xie, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

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

3:45 PM P4.5
Model Cilia - Actuable Polymeric Rods. R. Lloyd Carroll, S. Washburn and R. Superfine; Physics and Astronomy, University of North Carolina - Chapel Hill, Chapel Hill, North Carolina.

Ciliated cells are ubiquitous in biology. Understanding the dynamics of fluid flow in the vicinity of a beating cilium is critical to understanding and treating numerous human diseases, including the genetic disorder cystic fibrosis. We have fabricated magnetically-doped polymeric cilia-like structures, with dimensions and flexibility similar to those of a lung epithelial cilium ($\sim$0.8 μm diameter by $\sim$6 μm long). We will discuss details of the fabrication of the ciliated structures and present results of mechanical characterization. We will also discuss results derived from the actuation of the structures in a rhythmic beat pattern by means of controlled magnetic fields. The impact of this work on the understanding of fluid flow above ciliated cells and tissues and potential applications of such model systems will be described.

4:00 PM *P4.6
Mesoscopic Behaviour of the Molecular Motor-Cytoskeleton System. Jacques Prost, ESPCI, Paris Cedex 05, France.

Much of the cell mechanics, morphology and motility are determined by the dynamical properties of an actin network moving under the action of molecular motors and by treadmilling. The actin network constitutes a physical gel the cross-links of which are both temporary and mobile. I will show how one can write down a set of phenomenological equations, which can describe this situation. I will illustrate the usefulness of the equations by considering the behaviour of topological defects and in particular show under which circumstances they become mobile. I will eventually argue that such developments provide a useful paradigm for understanding cell motility such that of keratocytes. J.F. Joanny, F. Julicher, K. Kruse, J. Prost, K. Sekimoto, "Asters, Vortices, Spirals in active gels of polar filaments" in preparation.

4:30 PM *P4.7
Rapid analysis of DNA biopolymers using Nanopore based method. Amit Meller, Rowland Institute, Harvard University, Cambridge, Massachusetts.

The discovery that a voltage gradient can drive single-stranded DNA (ssDNA) or RNA molecules through a 2 nm trans-membrane channel, or a nanopore, has opened up the possibility of detecting and characterizing unlabelled polynucleotide molecules at low copy number using single channel recording techniques. It was found that the blockade signals produced by single polynucleotides traversing a narrow pore contain useful information about the biopolymer properties such as its sequence and secondary-structure, its length and type (for example RNA vs. ssDNA). In particular, the dynamics of the biopolymers characterized by their translocation duration times

were found to be a rich source of information, making it possible to discriminate "on the fly" between different types of polynucleotides in a mixture, and to detect single-base mismatches in short DNA hairpin molecules. Recently, we have enhanced the sensitivity of the nanopore detection technique by developed a method to rapidly modify the electric field applied on the charged polynucleotide while it is captured inside the pore1. This method allowed us to measure the unbiased channel-DNA interactions and to extend our measurements to DNA molecules that contain hairpin (base-paired) regions. Our method is capable of analyzing hundreds of individual molecules in a few minutes
time. 1. M. Bates, M. Burns, and A. Meller, Biophys. J. 84, 2366 (2003).

SESSION P5:
Chair: Ren Overney
Wednesday Morning, December 3, 2003
Room 309 (Hynes)

8:30 AM *P5.1
Exploring Reaction Pathways of Single Molecule Interactions through the Manipulation and Tracking of a Potential-Confined Microsphere. Wesley Philip Wong[1,3], Volkmar Heinrich[1] and Evan Evans[1,2]; [1]Biomedical Engineering, Boston University, Boston, Massachusetts; [2]Physics, Boston University, Boston, Massachusetts; [3]Physics, Harvard University, Cambridge, Massachusetts.

Weak non-covalent interactions between single molecules govern many aspects of microscopic biological structure and function (e.g. adhesion via receptor-ligand bonds, protein folding, molecular motors and mechanical enzymes, etc.). The dynamics of a "weak bond" are usually characterized by kinetic transport over an effective "energy landscape" defined along principal reaction coordinates. We present a new method to quantify subtle features of weak chemical transitions by analyzing the Brownian fluctuations of a functionalized microsphere held near to a reactive substrate. A weak external potential is used to confine the motion of the bead to a nanoscale domain and to apply a controlled bias field to the interaction. Stochastic interruptions in the bead dynamics report formation and release of bonds mediated by this "soft" energy confinement. In addition, exotic motions of a bead tethered to a reaction site on the substrate can be used to signal conformational changes such as the folding/unfolding of domains. Reaction pathways are mapped out by quantifying the statistics and rates of transition under controlled displacements of the confining potential. Experimentally, the three-dimensional motion of the bead is tracked using a reflection interference technique combined with high-speed video microscopy. In this way, the position of the bead can be measured with a lateral resolution of $\sim$3-5 nm and a vertical resolution of $\sim$1-2 nm at rates of over 100 times per second. Crucial to the interpretation of results, a Brownian-Dynamics simulation of the experiment has been developed to aid in the analysis of the statistics. This apparatus is designed to enlarge the scope of current techniques (e.g. Dynamic Force Spectroscopy [1]) to encompass near-equilibrium forward/reverse transitions of weak-complex interactions with one or more pathways. The method is currently being used to explore the barriers to formation of weak bonds and structural conformations, which have previously eluded definition. [1] Evans and Williams, In: Physics of Biomolecules and Cells. Ecoles des Houches d'Ete, LXXV. EDP Sciences - Springer Verlag, pp 145-185, 2002.

9:00 AM *P5.2
A New Look at Dynamic Force Spectroscopy of Adhesion Bonds. Joseph Klafter[1], Olga Dudko[1], Alexander Filippov[2] and Michael Urbakh[1]; [1]School of Chemistry, Tel Aviv University, Tel Aviv, Israel; [2]Donetsk Institute for Physics and Engineering of NASU, Donetsk, Ukraine.

Dynamic force spectroscopy of single molecules is described by a model which predicts a distribution of rupture forces, the corresponding mean rupture force and variance, all amenable to experimental tests. The distribution has a pronounced asymmetry which has recently been observed experimentally. The mean rupture force follows a (lnV)$\hat{}$2/3 dependence on the pulling velocity V and differs from earlier predictions. Interestingly, at low pulling velocities a rebinding process is obtained whose signature is an intermittent behavior of the spring force which delays the rupture. An extension to include conformational changes of the adhesion complex is proposed which leads to the possibility of bimodal distributions of rupture forces.

9:30 AM P5.3
Watering Silicon Nanograss: How to Get Droplets to Roll or Stick on Demand. Ashley Taylor[2], Tobias M. Schneider[1], Shu Yang[1] and Tom N Krupenkin[1]; [1]Bell Labs, Lucent Tech., Murray Hill, New Jersey; [2]New Jersey Nanotechnology Consortium, Murray Hill, New Jersey.

The interaction of liquids with solid surfaces is of great interest to many research areas ranging from biology and chemistry to physics and nanotechnology. Only recently studies have been expanded to include the interaction of liquids with nanostructured surfaces. In this work a dynamic electrical control of the wetting behavior of liquids on nanostructured surfaces, which spans the entire possible range from the superhydrophobic behavior to nearly complete wetting, has been demonstrated. We have demonstrated that the liquid droplet on a nanostructured surface exhibits sharp transitions between three possible wetting states as a function of applied voltage and liquid surface tension. We have examined experimentally and theoretically the nature of these transitions. The reported results provide novel methods of manipulating liquids at microscale. A wide range of applications, including micro- and nanofluidics, chemical microreactors, sensors, integrated thermal management in microelectronics, and optics communications may benefit substantially from the ability to dynamically tune the liquid-solid interactions.

10:15 AM *P5.4
Transverse Electrokinetic Effects in Microfluidics. Armand Ajdari, Physico-Chimie Theorique, ESPCI-CNRS, PARIS, France.

Fabricating microchannels with topographical patterns (with or without charge patterns) of simple symmetry permits the generation of transverse electrokinetic effects (electro-osmosis and streaming potential or currents) whereby a field applied along the channel generates an effect transverse to the channel or conversely. - Applications are proposed including (i) the local generation and control of the flow with low voltages using transverse electro-osmosis, and (ii) the local measurement of the flux of pressure-driven flow using transverse streaming potentials. - General Onsager relations are proven for these various effects, which extends the original derivation of Mazur and Overbeek linking EOF and streaming potentials in straight homogeneous channels. - We also report on experimental validation of these proposals in microfluidic systems made of microfabricated PDMS channels with patterned topographic modulations sealed against glass slides bearing microelectrodes.

10:45 AM P5.5
Abstract Withdrawn

11:00 AM P5.6
Anomalous Hydrodynamic Interactions in Confined Suspensions. Haim Diamant[1,2], Bianxiao Cui[2], Binhua Lin[2] and Stuart A. Rice[2]; [1]School of Chemistry, Tel Aviv University, Tel Aviv, Israel; [2]James Franck Institute, University of Chicago, Chicago, Illinois.

We study, experimentally and theoretically, the hydrodynamic interaction between colloidal particles confined between two plates (2D confinement) and in a linear channel (1D confinement). Several surprising anomalies are found compared to unbounded suspensions. (i) Despite the confinement, the coupling in 2D is long-ranged, decaying only as the inverse square of the inter-particle distance. (ii) In spite of this long-ranged coupling, two-particle dynamics in 2D confinement have an extremely weak dependence on suspension density. (iii) The transverse pair coupling in 2D confinement has a reversed sign, i.e., particles exert "anti-drag" on one another when moving perpendicular to their line of contact. (iv) The pair interaction in 1D confinement is short-ranged, decaying sharply to zero for distances larger than the channel width.

11:15 AM *P5.7
Control of Current Reversal and Separation of Particles In Inertia Ratchets. Fereydoon Family[1], H. A. Larrondo[2] and C. M. Arizmendi[1,2]; [1]Physics Department, Emory University, Atlanta, Georgia; [2]Depto. de Fisica, Facultad de Ingenieria, Universidad Nacional de Mar del Plata, Mar del Plata, Argentina.

We have studied the deterministic dynamics of underdamped single and multiparticle ratchets associated with current reversal, as a function of both the amplitude and the frequency of an external driving force. We show that control of current reversals in deterministic inertia ratchets is possible as a consequence of a locking process associated with different mean velocity attractors. Control processes employing small perturbations on the frequency and the amplitude of the external force may be designed in view of the intermixed fractal nature of the domains of attraction of the mean velocity attractors. The range where each control parameter reverses the current is determined. The influence of the mass of the particle is also considered in order to design control techniques capable of separating particles of different masses.

11:45 AM P5.8
Prediction of Transport Properties of Confined Nanosystems and Their Use for Virtual Fabrication of Nanomaterials.
Liudmila A Pozhar, MLBP, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

A fundamental, non-equilibrium statistical mechanical approach (functional perturbation theory, or FPT) derived by Pozhar and Gubbins (PG) has been used to elucidate relations between (1) the equilibrium structure, composition, chemistry and topology, and (2) the transport coefficients of nanosystems in confinement. Such relations have been obtained in terms of equilibrium structure properties (such as the density and correlation functions) calculated by means of equilibrium molecular dynamics (EMD) simulations. These data have been further used in the theoretical formulae to calculate diffusion and viscosity in the confined systems. The used theoretical formulae were obtained upon simplification of the fundamental PG expressions for the transport coefficients of inhomogeneous systems. The above theoretical studies suggest a fundamental, self-consistent, and at the same time, tractable and practical approach to virtual (i.e., theory-based, computational) processing of nanosystems to synthesize sub-nanostructured materials with pre-designed physical properties. This virtual synthesis concept is discussed in conjunction with experimental synthesis of silicon-based electronic nanomaterials, zeolites and particulate aggregations.

SESSION P6:
Chair: Joseph Klafter
Wednesday Afternoon, December 3, 2003
Room 309 (Hynes)

1:30 PM *P6.1
Dynamics of Water and Other Complex Fluids Under Molecular Confinement*. Jacob Klein, [1]Weizmann Institute, Rehovot, Israel; [2]Oxford University, Oxford, United Kingdom.

We have investigated the dynamic properties of water, of aqueous electrolytes, and of charged polymers (both adsorbed and brush-like, and also gelled) when the fluids are confined to films only a few molecules thick. Our results shed light on the frictional behaviour of such surfaces across the different complex fluids when they are rubbed past each other under strong compression. They reveal the important role of the hydration sheaths - about ions and about ionized monomers - in modulating such friction. Preliminary results have appeared in U. Raviv, P. Laurat and J. Klein, Nature 413, 51 (2001); U. Raviv and J. Klein, Science 297, 1540 (2002); and N. Kampf et al., Macromolecules, submitted (2003). * - with U. Raviv, N. Kampf, S. Giasson, J-F. Gohy and R. Jerome

2:00 PM *P6.2
Librational and Reorientational Motion of Confined Polar Liquids. Dean Venables[2] and Charles Schmuttenmaer[1]; [1]Chemistry, Yale University, New Haven, Connecticut; [2]National Metrology Laboratory, CSIR, Pretoria, South Africa.

The characteristics of the OH librational band of water and methanol confined within reverse micelles depend strongly on size. This collective librational motion exhibits a marked red-shift as a function of size from the bulk liquid to the smallest sized reverse micelle. The behavior over a large range of reverse micelle sizes for both systems is well described by a two-state model. However, one notable difference between the water/AOT/isooctane and methanol/AOT/isooctane systems is that the peak value of the extinction coefficient increases in going to smaller sizes for water, while it decreases for methanol, and the reasons for this will be discussed. The OH librational band of water and methanol in porous glasses will also be presented.

2:30 PM P6.3
Slippage of water confined between hydrophobic surfaces.
Cecile Marie Cottin-Bizonne, Elisabeth Charlaix, Lyderic Bocquet and Jean Louis Barrat; Bat, Leon Brillouin, Universite Claude Bernard, Lyon 1, Villeurbanne, France.

In hydrodynamics, the boundary condition for a flow at a solid wall is usually assumed to be a no-slip boundary bondition. If this condition describes quite well flows of simple liquids at a macroscopic scale, it is not necessary the case at smaller scales. Some theoretical, numerical and experimental arguments show that slip effects at the solid wall cannot be neglected in flows of confined liquids. The intensity of the slipage is caracterized by the slip length, defined as the position, inside the solid wall, at which the linear extrapolation of the velocity profile of the fluid vanishes. We first review the various experimental studies of slip effects of simple liquids on a variety of surfaces and show that there is a huge variability in the results obtained up to now. Then we present our experiments using a dynamic surface force apparatus. We measure the force exerted by a fluid confined between surfaces of various wettability as a function of the distance between the walls when the fluid is submitted to a dynamic shear. This measurement can be directly related to the slip length at the wall. We present more specifically results obtained with water confined between hydrophilic (low roughness pyrex) surfaces and hydrophobic (OTS grafted pyrex) surfaces. While a no-slip boundary condition is found on hydrophilic substrates, we observe slip effects on hydrophobic surfaces with the following characteristics : i) the hydrodynamic boundary condition is fully linear and does not depend on the shear rate nor on the gap between the surfaces in the range 0.5 to 500 s^{-1} for the shear rate and 0 to 200 nm for the gap ii) the hydrodynamic force is very well described by a slip length of twenty nanometers over the full range of experimental parameters, even in the limit of large gap and low shear. Our results are in strong contrast with those obtained by some other groups, using similar sytems and techniques, who report non-linear behaviour and absence of slip effect in the limit of large gap/low shear. However our results are in good qualitative and quantitative agreement with MD numerical simulations of confined fluids. We discuss some possible sources of experimental discrepancies in estimating the slip length at a solid wall in techniques based on hydrodynamic force measurements (SFA and modified AFM). References : Y. Zhu and S.Granick, Phys. Rev. Lett. 87(9) 096105, 2001 ; H. Spikes and S. Granick, Langmuir 19 5065-5071, 2003 E. Bonaccurso and H.-J. Butt and V. S. J. Craig, Phys. Rev. Lett. 90(14) 144501, 2003 O. I. Vinogradova and G. E. Yabukov, Langmuir 19 1227-1234, 2002 F. Restagno and J. Crassous and E. Charlaix and C. Cottin-Bizonne and M. Monchanin, Rev of Sci. Instruments, 73 (6), 2292-2298, 2002

3:15 PM *P6.4
Dynamics in Reverse Micelles. Nancy E Levinger, Chemistry, Colorado State University, Fort Collins, Colorado.

We have explored the dynamics occurring within the confines of reverse micelles using a range of methods. Recent results from solvation dynamics experiments, quasielastic neutron scattering and molecular dynamics simulations will be presented.

3:45 PM P6.5
Probing Colloidal Transitions by NMR Relaxometry: Interplay Between Confined Fluid Levy Dynamics and Particle Jamming. Pierre E. Levitz, PMC-Ecole Polytechnique, CNRS, Palaiseau, France.

Particle fluctuations in colloidal suspensions are generally considered to be much slower than the embedded fluid dynamics. It was recently proposed that the fluid self-diffusion nearby an interface follows a Levy statistics, extending the time domain of the confined fluid dynamics towards the low frequency range. It is then possible to probe colloidal particle motion and especially its evolution during a phase transition looking at the slow dynamics of the fluid molecule close to an particle surface. Using field cycling NMR relaxometry, we show how the slow and confined water dynamics at proximity of a colloidal surface provide an original way to follow the glass transition of a colloidal system made of plate-like Laponite particles, a synthetic clay. The interplay between fluid Levy dynamics and particle jamming is discussed. An analytical model involving correlated elementary water time steps on the colloidal interface is proposed and critically compared to our experimental data. The method permits to probe colloidal motions and especially their evolution during a phase transition in a non common way. In that sense, this method can be extended to other systems including mineral lyotropic liquid crystals and biological molecular structures.

4:00 PM P6.6
Adiabatic Compressibility of Water Confined In Reverse Micelles. Wladimir Urbach[1], J.Y. Le Huerou[2], M. Gindre[2], M. Waks[2], G. Bertho[3] and J.P. Girauil[3]; [1]LPS de l'ENS, CNRS UMR8550, Paris, France; [2]L.I.P., UMR CNRS 7623, Paris, France; [3]CNRSUMR8601, Paris, France.

We have investigated by high precision densimetry, ultrasound velocimetry and RMN reverse micelles of an anionic (AOT) and a non - ionic (C12E4) surfactant in decane, at increasing water concentration and at variable micellar volume fractions. Comparizon of the results reveals dissimilarities between the behavior of water in the non-ionic as well as the anionic surfactant. In the presence of AOT, the variation of the micellar compressibility vs. the surfactant polar headgroup area, can be represented by a linear variation with two different slopes from surfactant-to-water molar ratios Wo = 2 to 10 and above. For low Wo values (<10), if one assumes that the AOT molar fraction is close to unity, the micellar compresibility is very close to that of AOT monolayer. Above Wo = 10, which corresponds to the upper limit of bound water to the polar heads, the slope increases sharply indicating that the contribution of "free" water has to be taken into account. The variation of micellar compressibility vs.

Wo was interpreted by making use of effective medium theory and assuming a spherical shape of micelles. In the presence of AOT, the bound water (Wo range 2 to 10) layer thickness was determined by NMR ,The bound water compressibility is 54 10-11Pa-1. The water compressibility in the core of micelles 65 10-11 Pa -1. is significatively higher than bulk water compressibility (45 10-11 Pa -1.). As opposed to AOT, the variation of the micellar compressibility vs. the surfactant polar head group area is linear, In C12E4, between molar ratios of surfactant-to-water (Wo) 2 to 20, suggesting the presence at the same time of bound and free water, whatever the water volume fraction. In contrast to what has been observed in AOT reverse micelles, we cannot discriminate between the values of free and bound micellar water.

4:15 PM *P6.7
Vibrational Dynamics of the OH Stretching Mode of Water in Reverse Micelles Studied by Infrared Nonlinear Spectroscopy.
Hiroaki Maekawa[2], Kaoru Ohta[2] and Keisuke Tominaga[1,2,3];
[1]Molecular Photoscienec Research Center, Kobe University, Kobe, Japan; [2]Graduate School of Science and Technology, Kobe University, Kobe, Japan; [3]CREST/JST, Kobe, Japan.

Vibrational dynamics of the OH stretching vibration of water in the water pool of reverse micelles (aeorosol OT-100) are stuided by infrared nonlinear spectroscopy such as transient grating and three-pulse photon echo peak shift. The W0 value is changed from 2 to 40, which corresponds to a water pool diameter of a few A to about 20 A, respectively. Spectral diffusion, vibrational population relaxation, and energy transfer of the vibrational band will be discussed. Polarization-sensitive transient grating experiment shows rapid anisotropy decay of the OH stretching band, which is due to resonant energy transfer of the OH band. From the three-pulse photon echo peak shift experiment, the specrtal diffusion is dependent on the size of the reverse micelle.

4:45 PM P6.8
Thermal Expansion of Confined Aqueous Solutions.
Shuangyan Xu, Daniel J Sweeney and George Walter Scherer; Civil & Env Eng, Princeton University, Princeton, New Jersey.

Thermal expansion of the pore liquid in cement paste can produce destructive stresses, because the liquid expands much more than the solid matrix. The mismatch in expansion puts the liquid into compression and the solid into tension, leading to measureable dilatation of the body; if the saturated paste is heated and then held isothermally, the liquid drains from the pores and the body contracts to a dimension corresponding to the thermal expansion coefficient of the solid. This phenomenon can be used to measure the permeability of the paste - but it is of practical importance, because sudden heating (as in a fire) can produce cracks that raise the permeability and reduce the strength of concrete, even leading to structural failure. Recently we have demonstrated that the thermal expansion coefficient of the confined fluid is about 1.6 times as large as that of bulk water (or aqueous solution). In this paper, we will report systematic investigations of the expansion of water and salt solutions in porous glasses with controlled pore size, to evaluate the importance of the size of the hydrated ion relative to the pore size. The results will be used to interpret the behavior of pore liquid in cement paste.

SESSION P7: Poster Session:
Chairs: John Fourkas and Pierre Levitz
Wednesday Evening, December 3, 2003
8:00 PM
Exhibition Hall D (Hynes)

P7.1
Molecular Pumping and Separation in a Symmetric Channel.
Dana Lichtenberg[1], Alexander E Filippov[2] and Michael Urbakh[1];
[1]Department of Physical Chemistry, Tel-Aviv University, Ramat Aviv, Israel; [2]Donetsk Institute for Physics and Engineering of NASU, Donetsk, Ukraine.

A mechanism responsible for the directed transport and molecular separation in a symmetric channel is proposed. We found that under the action of spatial harmonic oscillations of the channel, the system exhibits a directed transport in either direction, presenting multiple current reversals as the amplitude and/or frequency of oscillations are varied. The particles of different masses may be forced to move with different velocities in the same or in the opposite directions by properly adjusting driving parametrs. The directed transport can be produced in both directions even in the absence of thermal noise, the latter can speed up or slow down the transport depending on the system parameters.

P7.2
Phase Separation of a Binary Liquid System in Controlled-Pore Glass.
Sebastian Schemmel[1], Gernot Rother[1], Annie Brulet[2], Thomas Hellweg[1] and Gerhard H. Findenegg[1];
[1]Stranski Laboratorium, Institut of Chemistry, Sekr. ER1, Technical University Berlin, Berlin, Germany; [2]Laboratoire Leon Brillouin, CEA-CNRS, Saclay, France.

Binary liquid mixtures separate into two phases of different compositions below a critical solution point. A porous medium affects the phase separation of a liquid mixture not only by geometrical confinement effects, but also by the preference of the pore surface for one component. In the one-phase region of the mixture, the latter will cause preferential adsorption, i.e., a concentration profile from the wall into the pore volume. In the two-phase region the walls will be wetted, either completely or partially, by the preferred phase, causing either a tube-like or a plug-like morphology of the preferred phase in cylindrical pores. In order to test some of these predictions, we have studied the structure and dynamics of the binary system iso-butyric acid (iBA) + heavy water (D_2O) in controlled-pore glass CPG-10-75 which comprises a mean pore size around 10 nm. Water is preferred by the pore wall in the iBA + D_2O system. The temperature-induced microphase separation of a mixture of 54 wt.-% iBA was studied over a wide temperature range (20 - 70°C), covering both the one-phase and the two-phase regions of the bulk system. Small-angle neutron scattering (SANS) was used to determine the structure of the liquid mixture in the pores. Concentration fluctuations in the one-phase region, which are expected to grow in size as approaching the two-phase boundary, are represented by an Ornstein-Zernicke (OZ) function with a correlation length ξ_C. Domains of the two phases, separated by sharp interfaces, are described by a squared OZ expression with a characteristic correlation length Γ_D. As expected, the correlation length of the diffuse concentration fluctuations in the one-phase region increases as the phase boundary is approached. A cut off, around 8 nm, is observed: it roughly corresponds to the average pore size. In the two-phases region ($T < 30°C$), these concentration fluctuations are replaced by the microphase-separated domains of the two phases, which slightly grow in size as one moves deeper into the two-phase region. The dynamics of fluctuations and microphase-separated domains have been investigated by neutron spin-echo (NSE) spectroscopy. NSE experiments yield the time dependence of the intermediate scattering function S(q,t). They can be fitted by a single-exponential decay, $S(q,t) \sim \exp(-\Gamma t)$, where Γ is the characteristic relaxation frequency which is related to the effective diffusion constant as $D_{eff} = \Gamma/q^2$. The observed decrease of D_{eff} with decreasing temperature is tentatively attributed to the increase of the size of the concentration fluctuations in the one-phase region and an immobilization of the domains at the pore surfaces in the low-temperature region. Both NSE and SANS studies show that the microphase separation of the liquid mixture in the porous matrix does not occur at a sharp temperature but extends over a wider temperature range below the phase separation temperature of the bulk mixture.

P7.3
Structure and Dynamics of Confined Alcohol and Polymer Melts as Determined by AFM.
Gexiao Sun, Michael Kappl and H.-J. Butt; Max-Planck-Institute for Polymer Reseach, Mainz, Germany.

To study the behavior of confined liquids, the force on a tip (as well as a sphere) over flat substrate first has been measured with atomic force microscope (AFM) in 1-propanol. Force jumps at small separations were observed with microfabricated tips and microspheres in 1-propanol on hydrophilic surfaces like freshly cleaved mica. The oscillatory force demonstrates that for the alcohol molecules it is energetically favorable to remain in the gap and form molecular layers. At relatively high approaching velocity the hydrodynamic force has been measured with a borosilicate glass sphere attached on a tipless AFM cantilever. A significant slip was observed. This indicates that boundary slip is a universal phenomenon even on lyophilic surfaces. Experiments have been extended to polymer melts (e.g. PDMS). The force profile between a silicon nitride tip and mica in monodisperse PDMS has been measured. A long-range repulsion and short-range oscillations were observed. The repulsion can be attributed to entropic interaction of polymer molecules in a confined gap and may be at least partly due to the viscous drag. The oscillations indicate layered structure of polymer molecules near solid surface. Results of other polymer melts on different surfaces are also discussed.

P7.4
Single Stranded DNA Translocation Through a Changing Structure Nanopore.
Ophir Flomenbom and Yossi Klafter; Chemical Physics, Tel -Aviv University, Tel -Aviv, Israel.

A study of a single stranded (ss) DNA translocation through a membrane channel is presented. Our model, based on the master

equation formalism, takes into consideration the effect of the ssDNA parts outside the membrane and its features within the membrane, on the first passage times (FPT) probability density function (pdf) of the translocation. We investigate the FPT pdf as a function of the ssDNA characteristics, such as the ssDNA length, composition and sequence, and as a function of the external field strength, and show that it can be mono or double peaked depending on the external field strength and the initial state of the translocation, or triple peaked, when fluctuation in the pore structure is introduced. The probability distribution function of the translocation times, in a free voltage environment, is shown to have two typical timescales, which differ by an order of magnitude. An analytical expression for the mean first passage time is computed, and in addition to numerical extracted characteristics of the FPT pdf, serves as a tool for the analysis of experimental observations.

P7.5
Electrowetting-based Open Microfluidic Systems.
Frieder Mugele, Stephan Herminghaus and Anke Klingner; Applied Physics, University of Ulm, Ulm, Germany.

Electrowetting is perhaps the most versatile technique for manipulating microscopic quantities of liquid on planar substrates. We outline a new concept for open microfluidic systems, which is based on the combination of chemical wettability patterns and patterned electrodes. We will describe three examples how electric fields and - in particular - the electrowetting effect can be used to manipulate liquid microstructures. 1) At sufficiently low voltage, within the so-called Lippmann regime, the liquid surfaces preserve their constant mean curvature in mechanical equilibrium. We demonstrate that morphological phase transitions between droplet-like and semi-cylindrical morphologies can be used to pump liquid efficiently between adjacent reservoirs. 2) At high voltage, in the saturation regime of electrowetting, instabilities of the contact line occur, which can also be exploited for the purpose of manipulating liquids. Making use of the balance between the Maxwell stress and the Laplace pressure, it is also possible to stabilize fluid microstructures with position-dependent mean curvature. 3) Finally, we demonstrate that capillary bridges spanning a slit pore between two planar surfaces can break and reform periodically due to a competition between electrowetting and electrostatic forces. These self-excited dynamics can be exploited to mix liquids in microfluidic applications.

P7.6
Retention of Liquids by Microporous Membranes.
John Charkoudian and Volkmar Thom; Membrane Technology Division, Millipore Corporation, Bedford, Massachusetts.

The interfacial and morphological factors controlling the confinement and support of liquids by microporous membranes were examined and analyzed using a model based on capillary pressure. Variables studied included surface composition, liquid surface tension, and pore structure. Micropores consisting of phase separated polyvinylidene fluoride (PVDF) and polyethersulfone (PES), and track etched polycarbonate (PCTE) were studied before and after surface modification for their ability to support columns of alcoholic aqueous solutions ranging in surface tension from 22 to 72 dynes/cm. Variation of average pore diameter within a class of polymer produced an inverse relationship between breakthrough pressure and pore diameter. For the unmodified surfaces, this pressure increased sharply when the liquid composition reached a critical surface tension value. Topography of surface pores also impacted confinement of liquids. AFM studies indicated that crater-like structures confined liquids to a greater extent than did volcano- like structures. Surface modification produced major effects on retention. Hydrophilizing monolayer coatings produced by in-situ polymerization of monomers in the PVDF series did not show the sharp increase in supported column height with increasing liquid surface tension observed for the unmodified membranes. These monolayers provided an additional breakthrough mechanism via liquid filled hydrogels. This mechanism was absent for the plasma modified PCTE series, which displayed the discontinuity observed for the unmodified counterpart. Based on the capillary model, scaling factors were calculated for each class of polymer. The PCTE series, having the most cylindrical pore geometry, displayed the lowest scaling factor, while the PES series showed the largest departure from ideality. Possible mechanisms are proposed to account for the resistance to leakage observed for the unmodified surfaces and the crater-like topographies.

P7.7
Diffusion on a Lattice in the Presence of Obstacles.
James Philip Lavine, Image Sensor Solutions, Eastman Kodak Company, Rochester, New York.

Results are presented for the diffusion of a particle on a square or cubic lattice in the presence of an obstacle. The first calculations are done in two dimensions, and the obstacle is a connected series of lattice sites that encloses an area with one lattice site permitting the particle to exit the confined area. The enclosed area is a small fraction of the model space, and the obstacle represents a membrane, a second phase, or a complex of atoms such as a cage. The diffusing particle cannot occupy an obstacle site, but it may remain at an adjacent site to simulate bonding. The diffusing particle starts within the confined area and undergoes a random walk on the lattice until it is captured by a boundary of the model space. In the absence of bonding, the mean time to capture is barely affected by the presence of the obstacle. However, the obstacle does influence the proportion of particles that reach each boundary. The side facing the exit receives the greatest portion of particles, and the opposite boundary receives the least portion. As expected, when bonding is allowed, the time to capture is increased. In addition, the survival time distribution requires more time steps before it decays in time with a single exponential. Variations on this model are also presented. These include an exit probability that varies with time and diffusion on a cubic lattice in three dimensions.

P7.8
Quasi Elastic Neutron Scattering Studies on the Molecular Motions of Methanol and Cyclohexane Adsorbed in MCM-41.
Subhankur Mitra[1], A.K. Tripathi[2], N.M. Gupta[2] and R. Mukhopadhyay[1]; [1]Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, India; [2]Applied Chemistry Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, India.

The sorption, binding, and the transport characteristics of various adsorbates in zeolitic pore systems have been investigated extensively, both experimentally and theoretically, with an objective to achieve the fundamental understanding of the behavior of guest-molecules in confined geometries. Using Quasi Elastic Neutron Scattering (QENS) techniques and in-situ Fourier Transform Infrared (FTIR) spectroscopy, we demonstrated recently that the benzene molecules existed in a highly compressed state, when occluded in the micropores of ZSM-type zeolites (Phys. Chem. Chem. Phys., 3, 4449 (2001)). In order to monitor the role played by the symmetry and the structure of the guest molecule, we have now undertaken QENS study on adsorption of cyclohexane and methanol in MCM-41 type of porous materials at room temperature. The QENS spectra show significant broadening from MCM-41 loaded with cyclohexane and methanol, whereas the dehydrated MCM-41 did not show any broadening over the resolution function of the instrument. Therefore the observed quasielastic (QE) broadening should be attributed exclusively to the molecular motions of guest molecules. Analysis of the data showed that the QE broadening corresponds to the translational motion of the guest molecules. It is also found that the methanol or cyclohexane molecule are performing jump diffusion with diffusion constant $1.47 \times 10^{-5}$and 1.68×10^{-5} cm^2/sec respectively inside the pores of MCM-41. On comparing this diffusivity with the value reported for the diffusion constant of liquid cyclohexane at 298 K ($D = 1.70 \times 10^{-5}$ cm^2/sec), and liquid methanol at 298 K ($D \sim 2.5 \times 10^{-5} cm^2$/sec) we may conclude that the translational diffusion constant of cyclohexane in MCM-41 is of the same order as that of bulk liquid cyclohexane. However, the translational diffusion constant of methanol in MCM-41 is much less than that of bulk liquid methanol.

P7.9
A Slope-dependent Disjoining Pressure for Non-zero Contact Angles. Qingfang Wu and Harris Wong; Mechanical Engineering Dept., LSU, Baton Rouge, Louisiana.

A thin liquid film experiences additional intermolecular forces when the film thickness h is less than roughly 100 nm. 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. A recent ad hoc derivation including the slope hx leads to a P = P(h, hx) that allows non-zero contact angles, but it permits a contact line to move without slip. This work derives a new disjoining-pressure expression by minimizing the total energy of a drop on a solid substrate. 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 gives in the small-slope limit P = P(h, hx, hxx). The term containing the curvature hxx is new; it prevents a contact line from moving without slip. Equilibrium drop and meniscus profiles are calculated for both positive and negative disjoining pressure. Evolution of a film step is solved by a finite-difference method with the new disjoining pressure included; it is found that hxx = 0 at the contact line is sufficient to specify the contact angle.

P7.10
Simulation of Polymeric Membrane Formation by Immersion Precipitation: Liquid-liquid Demixing. Bo Zhou and Adam Powell; Daterials Science and Engineering, M.I.T., Cambridge, Massachusetts.

Most commercial microporous membranes, which enjoy widespread use in filtration and purification, are made by the immersion precipitation process. This process begins with liquid-liquid demixing of a non-solvent/solvent/polymer ternary system into polymer-rich and polymer-lean phases; this demixing step determines much of the final morphology. In this work, a ternary Cahn-Hilliard formulation incorporating a Flory-Huggins homogeneous free energy function and coupled with variable-viscosity interface-driven fluid flow is used to simulate phase separation during liquid-liquid demixing. Simulations begin with uniform initial condition with a small random fluctuation to simulate spinodal decomposition, and also with a two-layer polymer/solvent/nonsolvent initial condition to simulate actual membrane fabrication conditions. 2-D and 3-D simulation results are presented which demonstrate the effects of M_p (degree of polymerization), K_{ij} (gradient penalty coefficients) and χ_{ij} (Flory-Huggins interaction parameters) on phase separation behavior.

P7.11
Relaxation And Aging Effects in Suspensions of Silica Particles. Seila Selimovic and Yue Hu; Physics, Wellesley College, Wellesley, Massachusetts.

In our study of the relaxation and aging phenomena in silica suspensions we have subjected several suspensions of silica particles in silicone oil and water to different shears and stresses. We find that the oily samples, initially of a pasty consistence, age in a period of 2 weeks. Samples containing a Methyl-Siloxane-Dimethylsiloxane copolymer have a longer aging period. Aqueous samples age much faster. After their respective aging period all samples are nearly Newtonian and flow very well. The relaxation measurements conducted 1 week after the mixing of the oily samples show that the elasticity rises with shear, resulting in a destruction of previously present structures, which enables the silica particles to build new, gel-like networks. Aqueous samples, however, do not show such effects. We will discuss a possible mechanism for this aging and relaxation behavior. * This work has been supported by a Radcliffe Fellowship, a National Science Foundation grant (no. DMR-9971432), and a Wellesley College Summer Research Fellowship. We also acknowledge the use of lab facilities provided by D. A. Weitz of Harvard University.

P7.12
Effect of Different Layer Thicknesses and Boundary Conditions of Confined Liquid Crystal On Dynamics of Director Relaxation: Dynamic Light Scattering Investigations. Sarmistha Basu and Fouad M Aliev; Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

Dynamic light scattering (DLS) method was applied to study the boundary conditions (planar-axial and homeotropic-radial) and layer thickness of liquid crystal (8CB) confined to cylindrical pores influence on phase transitions and relaxation of director orientational fluctuations. For confined 8CB in the nematic phase two well-defined relaxation processes were observed in DLS experiments 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. The slow decay is more pronounced in the treated samples than in non-treated samples. 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 relaxation times of the first process (bulk-like) decrease with the decrease of the thickness of the surface layer, however for each thickness it is almost temperature independent in a wide temperature range corresponding to nematic phase. 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.

P7.13
Collective and Molecular Dielectric Relaxation In Confined Liquid Crystals: Effect of Different Layer Thicknesses and Boundary Conditions. Fouad M Aliev and Manuel Rivera Bengoechea; Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

Broadband dielectric spectroscopy (DS) was applied to study the influence of boundary conditions (planar-axial and homeotropic-radial) and layer thicknesses of liquid crystal confined to cylindrical pores on low frequency and high frequency dielectric relaxation processes. The low frequency measurements provide information about the relaxation of surface polarization that arises at the liquid crystal - pore wall interface. Information about reorientational dynamics of molecular origin is obtained in high frequency experiments. The homeotropic alignment of molecules facilitates the investigation of the librational mode using DS at high frequencies. We found that the behavior of this mode is totally different from the behavior observed in investigations of relaxation resulting from reorientation of molecules around their short axis. The temperature dependence of relaxation times of librational mode could not be described by the Arrhenius law. Instead the interpretation of the results obtained in nematic phase needs the involvement of temperature dependence of orientational order parameter. In the smectic-A phase and the supercooled state the temperature dependence of relaxation times is mainly determined by the variations of viscosity. The broadening of dielectric spectra is observed in confined LC. The broadening increases with decrease of liquid crystal layer thickness. The spectra of all samples with axial orientation of molecules consist of the main peak due to the reorientation of molecules around short axis (characteristic frequency fm $\sim$ 5 MHz). In these samples is detected the secondary peak (fm $\sim$ 50 MHz) of much smaller amplitude. The relative contribution of this relaxation process increases with the decrease of the thickness of the LC layer. The main relaxation process broadens and its relaxation times decrease with decreasing thickness. The low frequency dielectric relaxation is compared to relaxation investigated in dynamic light scattering experiments. A detailed description of the results of the low frequency relaxation of surface induced polarization for all samples will be presented.

P7.14
Gold Nanoparticles as Probes of Nanoscale Thermal Transport in Aqueous Systems. Zhenbin Ge, Scott Huxtable, David G. Cahill and Paul V. Braun; Department of Materials Science and Engineering, UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN, Urbana, Illinois.

The thermal conductance, G, of the gold nanoparticle/fluid interface has been determined for tiopronin functionalized $\sim$5nm gold nanoparticles in both water and water-DMSO mixtures. These particles have been investigated as probes of thermal transport in nanoparticle containing aqueous solutions. Subpicosecond λ=770 nm optical pulses from a Ti:sapphire mode-locked laser are used to heat the particles and their temperature decay are interrogated through time-resolved changes in optical absorption of the solution. Approximate values of the thermal conductance G of the nanoparticle/fluid interfaces are determined by fitting the data with modeling of heat flow across the nanoparticles/fluid interfaces and through the surrounding fluid. The thermal decay of pure Au nanoparticles in aqueous solution at short time (less than 10ps) is partially obscured by electronic effects; from our preliminary results, we set a lower limit G > 100 MW m-2 K-1, approximately an order of magnitude larger than the alkanethiol-terminated Au nanoparticles in organic solvents. Mixing water with DMSO increases the transient absorption probably due to the larger refractive index of DMSO. We have previously shown that Pd-doped Au nanoparticles in organic solvent have a much larger transient absorption than pure gold nanoparticles. We are currently investigating the synthesis and properties of Au alloy nanoparticles in aqueous systems. We will measure G for Tiopronin and PEO functionalized gold nanoparticles in aqueous solution to evaluate the effect of chemical functionality of the surface on G.

P7.15
Anomalous kinetics of early time growth of depletion zone inside and outside of a trap with one-dimensional geometry. Hailin Peng, Sung-Hyun Park and Raoul Kopelman; Univ of Michigan, Ann Arbor, Michigan.

We studied the kinetics of growth of depletion zone near a single static line trap in an effective one-dimensional geometry by experiment, Monte Carlo simulation and exact enumeration calculations. The experiment is based on the photobleaching reaction of fluorescein dye. Fluorescein dye solution is confined into a 150-mm-thick chamber. A laser beam serves as a phototrap. We monitored the fluorescence intensity around the trap at different times. The main parameter of interest is the theta-distance, which is related to the expansion of the depletion zone and can be measured directly from experiment. We found out that we had theta-distance scales with $\hat{t}(1/2)$ asymptotically, as predicted by previous theory. In addition, we found out that the q-distance increases faster than $\hat{t}(1/2)$ inside and outside of the trap at early times, which has not been explored previously. And we studied the trapping strength effect by

changing the power of the laser beam. Our experimental results are consist with our simulation and enumeration results. The latter two show that the asymptotic results for an exact 1-dimensional lattice are still valid in a quasi-1-dimensional system, for both perfect and imperfect trapping reactions.

P7.16
Abstract Withdrawn

P7.17
Effects of Surface Roughness, at Nanometric Scales, on the Friction at Simple Fluids Solid Interfaces. Tatiana Schmatko, Hubert Hervet and Liliane Leger; Physique de Fluides Organises, College de France, Paris.

We have developed in the past few years an optical technique named Near Field Laser Velocimetry (NFLV) based on fluorescence recovery after photobleaching and excitation of the fluorescence by evanescent waves, allowing to characterize the flow velocity profile in the very vicinity of a solid surface without perturbing the flow lines. We have thus shown that a simple fluid like hexadecane was able to develop flow with slip at the wall, with a slip length much larger than the molecular size, provided the solid surface was smooth enough. We shall present systematic experiments aimed to establish the role played by the surface roughness in decreasing the aptitude of the liquid to develop slip at the wall (i.e. in increasing the friction). To do so, we have used NFLV and hexadecane, and we have developed ways of forming surfaces with controlled roughness, at nanometric scales. This could be achieved by grafting on a smooth highly polished sapphire surface (rms roughness 0.5 nm, as seen through X rays reflectivity techniques) hyperbranched polymer molecules, acting as nanoparticules attached to the surface. Both the size of the nanoparticules and their surface densities could be controlled through the parameters of the grafting reaction and the size of the initial polymer molecules. For rather low surface densities, the surface roughness induced by the grafted nanoparticules decreases the slip length. Results in terms of slip length as a function of the lateral and vertical scales of the surface roughness will be compared to recent models on the role of surface roughness on friction.

P7.18
Diffusion and Dynamics in Thin Films. Christopher L. Soles[1], Bryan D. Vogt[1], Vivek M. Prabhu[1], Ronald L. Jones[1], Eric K. Lin[1], Wen-li Wu[1], Dario L. Goldfarb[2] and Marie Angelopoulos[2]; [1]Polymers Division, NIST, Gaithersburg, Maryland; [2]Advanced Lithography Team, IBM TJ Watson Research Center, Yorktown Heights, New York.

Diffusion is of paramount importance in chemically amplified photoresists, affecting processes diverse as deprotection through the mobility of the photoacids and dissolution through the diffusivity of the aqueous developer into the resist film. In this presentation we quantify deviations in the diffusive properties as a function of film thickness and relate these changes to native dynamics of the polymer film. These dynamics are quantified via incoherent neutron scattering in terms of an average mean-square atomic displacement on a time scale of approximately 200 MHz and faster. Acid mobility measurements are made through model bilayer experiments whereby photoacids from a feeder layer diffuse into and induce deprotection in a resist underlayer. As the resist thickness decreases below 50 nm, so does the photoacid mobility. Likewise, quartz crystal microbalance studies are used to track the diffusion of moisture into dry resist films as a function thickness. There is a concomitant decrease in the moisture diffusivity with the reduced acid mobility and we correlate both of these phenomena to a decrease in the native dynamics of the polymer film. Practical examples with relevance to current lithography techniques will be given.

P7.19
Diffusive Entwining Of Two Fluid Phases In Chemically Patterned Microchannels. Olga Kuksenok[1], David Jasnow[2] and Anna Balazs[1]; [1]Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania; [2]Physics Department, University of Pittsburgh, Pittsburgh, Pennsylvania.

Via a coarse-grained model, we simulate the flow of a pressure driven binary AB fluid through a three dimensional microchannel, which is decorated on both top and bottom with distinct A- and B-like patches. The advection is "frustrated" because A-like patches (that attract the A- component) are placed in the path of the B stream and similarly, B-like patches are placed in the path of the A fluid. A competition between two factors, the advection caused by the imposed flow and the interactions between the confined fluids and patterned substrate, introduces non-linearity into the system. This non-linear behavior gives rise to a temporally periodic state, where the A and B fluids are intertwined. Through a simple scaling analysis, we estimate the dependences of the spatial and temporal periods on the systems parameters (the length of the patterned region, the value of the imposed pressure gradient and the interfacial tension between A and B fluids); these estimates are in good agreement with the simulations results. In effect, the simple pattern of chemically distinct patches introduces positive feedback, which is responsible for the instability of the interfaces of the injected fluids.

P7.20
Slow Relaxation of Poly(methyl methacrylate) Confined in Thin Films. Helen Richardson, Joseph L Keddie and Michele Sferrazza; Dept Physics, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom.

Glassy polymer films spin-cast from solution have many important technological applications including lithography, nanotechnology and optical coatings. Moreover, they are important from a fundamental standpoint because they constitute highly metastable forms of soft matter in a confined state[1]. As solvent evaporates from a spin-cast film, the glass transition temperature, T_g, of the polymer solution increases. When the T_g becomes equal to the temperature of the experiment, the solution vitrifies, and the rigidity acquired by the film opposes further solvent loss[1,2]. The polymer concentration at the vitrification point, ϕ_g , can be adjusted by varying the polymer molecular mass and by using polymers of different structural isomers. Ellipsometry and quartz crystal microgravimetry are used to measure simultaneously the changes in thickness and mass in spin-cast poly(methyl methacrylate) thin films as a function of time. By combining the data from the two techniques, the polymer's structural relaxation and solvent loss are probed from within a few minutes to many days after spin-casting. The results show a linear correlation between solvent loss and change in film thickness for a period up to 20 hours. Thereafter, the rate of solvent loss rapidly decreases, whereas the rate of change in thickness decreases more slowly over a period of days. This suggests that at later times, the polymer glass is undergoing structural relaxation without simultaneous solvent loss. The rate of volume relaxation in thin films is an indicator of polymer mobility. A study of the effects of temperature and ageing time on the relaxation can therefore provide useful insight into polymer dynamics in confinement[3]. Our previous work[4] has found anomalous expansivity-temperature behaviour for spin-cast PMMA, with a negative expansivity attributed to volume relaxation and with very slow relaxation occuring while ageing at room temperature. We extend this study to examine relaxation in spin-cast films as a function of film thickness at various temperatures. The data are considered in relation to the Kohlrausch-Williams-Watts model to obtain information on the distribution of relaxation times. This distribution, in turn, will be discussed in relation to the different modes of relaxation of the polymer near an interface in the confined state versus that in the "bulk" state. [1] G. Reiter and P.G. de Gennes, Eur.Phys.J.E, 6, (2001) 25-28. [2] L. Liebler and K. Sekimoto, Macromolecules, 26, (1993) 6937-6939. [3] S. Kawana and R.A.L. Jones, Eur.Phys.J.E, 10, (2003) 223-230. [4] H. Richardson, M. Sferrazza, and J.L. Keddie, Eur.Phys.J.E. Direct, in press

P7.21
A new method to determine the glass transition in thin polymer films via charging in XPS. Joern Erichsen, Kai Dolgner, Vladimir Zaporojtchenko and Franz Faupel; Chair for Multicomponent Materials, Christian-Albrechts University, Kiel, Germany.

X-ray photoelectron spectroscopy (XPS) spectra of dielectric materials have a shift due to charging of the specimen. If polymer films are annealed above the glass transition (Tg), then the shift decreases. We will show that this effect is correlated to glass transition in the bulk of the polymer films for different polymers as well as for different molecular masses for polystyrenes. This effect can be used to determine the bulk Tg of thin polymeric films. For comparison we will present surface Tg results of the same films determined by the embedding of noble metal nanoclusters [1]. [1] V. Zaporojtchenko, T. Strunskus, J. Erichsen, F. Faupel, Macromolecules, 34(5) (2001) 1125.

P7.22
Phase transitions on Pb/Ge(001) thin films. Fulvio Ratto[1,2], Alberto Morgante[2,3], Luca Floreano[2], Dean Cvetko[2,4] and Gregor Bavdek[2,4]; [1]EMT, INRS, Varennes, Quebec, Canada; [2]TASC, INFM, Trieste, Italy; [3]Dipartimento di Fisica, Universita' di Trieste, Trieste, Italy; [4]Jozef Stefan Institute, University of Ljubljana, Ljubljana, Slovenia.

During the last decades an intense effort has been devoted to the characterization of the phase transitions observed in thin metallic layers deposited on semiconducting substrates. In particular, the Pb/Ge interfaces have always been attracting a particular interest, as they have been considered as a model system for the singling out and characterization of the elements determining the Schottky barrier height. Nevertheless, due to the theoretical possibility for anomalous

structural phase transitions, namely charge density waves (CDWs) [1], most of the attention has recently been focused on the merely scientific studies. Although nearly no experimental evidence has been reported supporting the CDW picture [2], the nature and origin of phase transitions in thin metal films still feeds an opened and challenging debate [3]. We propose a complete thermodynamical characterization of the low temperature phase transitions observed in Pb/Ge(001) mono-atomic films, performed by helium atom scattering (HAS), and mainly based on the theoretical frame developed for the surface disordering processes [4]. We show that the HAS technique can lead to a convincing determination of the universality class of the observed phase transition, accounting for the observed symmetry increase with the temperature. Further, we show a simple way to exploit the HAS properties, in order to observe the eventual occurrence of local corrugation modifications, predicted by the CDW theory [5]. A discussion of the limits imposed by the scattering approach, together with the need for the adoption of complementary techniques, is finally presented. [1] J. M. Carpinelli, H. H. Weitering, E. W. Plummer, R. Stumpf, Nature, 381, 398 (1996); [2] L. Floreano, D. Cvetko, G. Bavdek, M. Benes, A. Morgante, Phis. Rev. B, 64, 075405 (2001); [3] F. Ratto, MSc Thesis in Physics (2002); [4] B. N. J. Persson, Surf. Sci. Rep., 15, 1 (1992); [5] T. Aruga, J. Phys. C. M., 14, 8393 (2002).

P7.23
Dimensional crossover in the growth of the depletion zone in an effective 2D geometry: experiments and Monte Carlo simulations. Sung Hyun Park[1], Hailin Peng[1], Panos Argyrakis[2], Haim Taitelbaum[3] and Raoul Kopelman[1]; [1]Department of Chemistry, University of Michigan, Ann Arbor, Michigan; [2]Department of Physics, University of Thessaloniki, Thessaloniki, Greece; [3]Department of Physics, Bar-Ilan University, Ramat-Gan, Israel.

The kinetics of the growth of depletion zone around a static trap in an effective two-dimensional geometry was studied using a photobleaching experiment of fluorescein dye by a focused laser beam. The experimental results confirm the theoretical non-universal scaling for the growth of the depletion zone at the asymptotic limit. The finite trap size and the imperfect trapping strength are found to generate an anomalous early-time behavior in the growth of the depletion zone inside the trap. The dimensional crossover behavior from 2D to 1D was observed due to the finite width of the reaction zone. The crossover time is found to scale with the width of the rectangular reactor. Monte Carlo simulations and exact enumeration were performed to support the experimental results. Similar dimensional crossover behaviors from 3D to 1D and even from 3D to 2D to 1D are discussed for the trapping reactions in three dimensional space.

P7.24
Abstract Withdrawn

P7.25
Homogeneous and heterogeneous crystallisation of poly(ethylene oxide) confined to droplets: the dependence of the crystal nucleation rate on length-scale. Michael Massa and Kari Dalnoki-Veress; Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada.

We present a study of homogeneous and heterogeneous nucleation in polymer crystallisation. In bulk samples the crystallization is typically dominated by nucleation from defects (heterogeneous nucleation). Consequently, studies of nucleation initiated by the polymer itself (homogeneous nucleation) must rely on sample preparation to minimize this effect. We present a study of nucleation within discrete droplets of poly(ethylene oxide) that are formed by the dewetting of a thin film on an unfavourable substrate. The samples provide an ensemble of impurity-free droplets, with length-scales that can easily be measured. Droplet crystallisation is observed in two distinct temperature regimes. The data for low supercooling (heterogeneous) and high supercooling (homogenous) nucleation events are qualitatively different, and reflect the fundamental differences of these two nucleation processes. We show that the crystallisation which occurs at high supercoolings ($\Delta T > 65$ K) has a nucleation rate which scales with the volume of the domain, indicating that we are observing homogeneous nucleation in the bulk of the droplets, rather than a surface-nucleated process. Furthermore, we observe a strong temperature-dependence in the nucleation rate for impurity free droplets. The experiments presented here provide a simple method that can be used to study heterogeneous and homogeneous nucleation in great detail.

P7.26
Phase-field Modeling of Solidification in a Confined Spherical Nano-Particle. Julia Slutsker[1], Geoffrey B. McFadden[1], Alexander L. Roytburd[2], William J. Boettinger[1] and James A. Warren[1]; [1]NIST, Gaithersburg, Maryland; [2]University of Maryland, College Park, Maryland.

The phase field model of the non-isothermal solidification taking into account the stress field is proposed. This model has been applied to the kinetics of melting and solidification in confined sphere. The complete numerical solutions taking into account the time-space evolution of temperature, order parameter and stress field has been obtained. It has been shown that at some boundary and initial conditions the evolution results in steady states corresponding time-independent distribution of order parameter and uniform temperature. The value of interface energy has been estimated by comparing the phase fraction in the steady states with the equilibrium following from the sharp-interface model. It has been shown that at small radiuses of sphere the equilibrium two-phase states significantly shifted and their unstability appears due to effect of interface energy. This effect is particularly significant if the radius of sphere on the nano-scale level is considered.

P7.27
Abstract Withdrawn

P7.28
Theoretical Modeling of Interfacial co-Polymerization. Victor V. Yashin, Olga Kuksenok and Anna C. Balazs; Chemical & Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

We present a theoretical description of the formation of a thin polymeric layer at an interface between two immiscible low molecular weight liquids in the process of interfacial co-polymerization. This technique is used to synthesize various macromolecules. We consider a simplistic model in which an alternating copolymer AB forms at the interface between phase separated low-molecular species A and B. It is assumed that any A(B) unit can be reversibly attached to any available B(A) unit or B(A)-ended chain with no intermediate activation process involved. Although the co-polymerization process is considered to be reversible in general, the forward reaction is assumed to be much faster that the backward one. Description of the formation of the copolymer layer is provided by a system of reaction-diffusion equations, which describe the chemical evolution and diffusive dynamics of the polydisperse mixture of AB-copolymers around the interface, and the evolution of the interface itself. Kinetics of the layer formation is studied under the simplifying assumption that the rate of chain growth is small in comparison with the rate of interdiffusion so a quasi-equilibrium can be achieved. The equilibrium structural characteristics of the formed polymeric layer are obtained using a self-consistent field theory approach. The effects of the chemical reaction rates and the interaction parameters on the kinetics of formation and the equilibrium structure of the AB-copolymer layer are demonstrated and discussed.

P7.29
Terahertz Radiation Spectroscopy on Chloroform Confined in Porous Silica Glasses. Kohji Yamamoto[1], Taku Sato[2], Hiroaki Okuno[2], Keisuke Tominaga[1,2,3], Shinji Saito[4], Brian J. Loughnane[5], Alessandra Scodinu[5] and John T. Fourkas[5]; [1]Molecular Photoscienec Research Center, Kobe University, Kobe, Japan; [2]Graduate School of Science and Technology, Kobe University, Kobe, Japan; [3]CREST/JST, Kobe, Japan; [4]Faculty of Science, Nagoya University, Nagoya, Japan; [5]Department of Chemistry, Boston College, Chestnut Hill, Massachusetts.

Refractive indices and absorption coefficients in the far infrared (IR) region of chloroform confined in porous silica glasses are measured by terahertz (THz) radiation spectroscopy. The pore size of the glass is changed from 24 A to 91A. The far IR absorption spectra are measured in the frequency region from about 15cm-1 to 70 cm-1. The spectra of chloroform in all the glasses are different from that in a bulk liquid. The bulk spectrum shows a peak at around 40 cm-1. However, in the glasses the spectral intensity monotonically decreases as a function of frequency. The low-frequency Raman spectra of chloroform in the porous silica glasses were measured by optical Kerr effect spectroscopy, and the pore-size dependence of the spectrum was rationalized in terms of a two-state model, where the liquid molecule was assumed to exist in two different sites, a region near surface and a region like bulk. This two-state model is applied to interpret the size-dependence of the far IR spectrum. We have found that it is necessary to assume a large value of $<M(0)M(0)>$ in the porous silica glasses compared to that in the bulk, where M(t) is the time dependent total dipole moment of the system. This may suggest that the dipoles near surface align each other regularly due to their electrostatic interaction.

P7.30
Application of Molecular Modeling to Nanofluidics: Designing Smart Flow-Control Valves Based on Stretch-Collapse Transitions of Grafted Polymers. Shashishekar P Adiga and Donald W Brenner; Materials Science and Engineering, North

Carolina State University, Raleigh, North Carolina.

Recently there has been a great interest in utilizing stretch-collapse transitions in grafted polymer layers to regulate fluid flow through nanopores. By choosing an appropriate polymer-solvent system that opens and closes the pore in response to environmental variables, one could envision designing a smart flow-control valve with a variety of potential applications including molecular sorting, smart drug delivery and ultrafiltration. In this paper we will discuss the application of polymer physics and molecular dynamics simulations to the design of such a system. In particular, we have calculated solvent flow rates through a cylindrical nanopore grafted with polymer chains in a poor and a good solvent. The simulations demonstrate that in a good solvent, the grafted chains are in a stretched state, offering resistance to flow and when exposed to a poor solvent undergo a collapse transition, increasing the pore size. To determine the validity of continuum calculations based on porous layer model, we have calculated the permeability of the pore over a range of solvent quality and compared it with the simulation results. The flow rate through the pore was determined by solving the Brinkman equation that treats the grafted layer as a porous medium. The calculations required permeability of the solvent into the polymer chains, which is related to polymer density profile inside the pore through some porous layer model. The polymer density profile was determined by a self-consistent approach for different values of solvent quality. The simulations provided useful insights in determining the most appropriate porous layer model to be used under different solvent conditions. For example, in a poor solvent, the grafted chains form pinned micelles comprising several chains, giving rise to a spatial variation in polymer density along the axis of the pore. This work was supported by a grant from the NASA-Ames Research Center.

P7.31
Modelling two-phase flow in microfluidic devices.
Mario De Menech, Unilever R&D, Vlaardingen, Netherlands.

A phase-field method is used to model two-phase flow in microfluidic devices, where capillary and viscous stresses dominate over inertial forces. Dissipative and reactive couplings in the hydrodynamic equations are derived from a Cahn-Hilliard-van der Waals free energy, which accounts for the equilibrium thermodynamics of the fluid system, including phase behaviour, interfacial tension and wetting properties. The singularities inherent to the free-boundary description are smoothed out by the presence of a diffuse interface over which interfacial stresses are distributed, such that complex phenomena like droplet breakup and coalescence or contact line dynamics can be resolved numerically. The reliability of the scheme used to solve the discretized transport equations is tested against different benchmarks for free flow conditions. The model is then applied to the simulation of the flow of droplets in microdevices, resulting in a satisfactory agreement with the behaviour observed in experiments.

P7.32
Dynamics of Excess Water in Hydrotalcite. Subhankur Mitra[1], A. Pramanik[2], D. Chakrabarty[2] and R. Mukhopadhyay[1]; [1]Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, India; [2]Hindustan Liver Research Centre, Andheri, Mumbai, Maharashtra, India.

Layered double hydroxides (LDHs), also known as mixed-metal layered hydroxides are important class of materials. Hydrotalcite in this class of materials can be described by the formula $Mg_6Al_2(OH)_{16}CO_3.\ 4H_2O$. The cations are octahedrally linked to each other through hydroxide groups to form a brucite like sheets of metal hydroxides with interlayer regions occupied by anions and water molecules. The layered sheet is referred to as host layer and anions and water molecules constitute the guest layer. Interest in hydrotalcite like compounds arises mainly because of its formation during the synthesis of mixed oxide catalysts via the coprecipitation route. Due to structural limitations attributable to various LDH site defects, the guest layer structure and particularly the dynamics of the anions and water are not fully understood. We have studied the dynamics of excess water inside hydrotalcite layers using Quasi Elastic Neutron Scattering (QENS) technique. Hydrotalcite with 30%, 50% and 9% of excess water ($Mg_6Al_2(OH)_{16}CO_3.\ 4H_2O$+x.$H_2O$) is studied by QENS technique. Hydrotalcite with no or very little excess water ($Mg_6Al_2(OH)_{16}CO_3.\ 4H_2O$) showed no quasielastic broadening over the instrumental resolution (ΔE=200 μeV) suggesting no motion of water molecules occurring in the time scale of 10^{-10}-10^{-12} psec. However, quasielastic broadening is seen in 9%, 30% and 50% excess water sample. The QENS spectra of excess water sample is fitted with a scattering function which consists both rotational and translation motion of water molecules. Rotational diffusion constant D_R obtained from the fitting is found to be 0.1 meV for all the excess water samples. This value of rotational diffusivity is very close to that of bulk liquid water at room temperature. Variation of Half Width at Half Maximum (HWHM) of the translational component with $Q^2$is found to follow the random translational jump diffusion model. Translational diffusion constants obtained for 9%, 30% and 50% excess water are 1.1×10^{-5}, 1.9×10^{-5} and 2.1×10^{-5} cm^2/sec respectively. It is found that the translational diffusivity decreases with the decrease of the amount of excess water. This is mainly due to the fact that when the amount of excess water is small they are mostly bound to the host layer. With increase amount of the excess water more and more of the water molecules are available away from the layer surface and are relatively free.

P7.33
Boundary Conditions for Multi-component Fluids: Implications for Nanodevices and Spreading. Colin Denniston[1,2] and Mark O Robbins[1]; [1]Physics and Astronomy, Johns Hopkins Univ., Baltimore, Maryland; [2]Applied Mathematics, Univ. Western Ontario, London, Ontario, Canada.

We examine flow of multi-component fluids near solid interfaces using molecular dynamics. Concentration gradients can produce flow profiles that are inconsistent with all commonly used macroscopic boundary conditions. When combined with differential wetting of confining solids, these concentration gradients drive convective flows that can power nanopumps or motors. These effects can be described by a new set of boundary conditions that allow continuum equations to be applied down to molecular scales. Implications for nanodevices and the effects of concentration gradients on dynamic contact angles will be described.

P7.34
Dynamics and Structure of Smectic Liquid Crystal Multilayers at the Air-Water Interface. Lu Zou[1], Prem Basnet[1], Ji Wang[1], Violeta J Beleva[1], Andrew J. Bernoff[2], James C Alexander[3], J. Adin Mann[4] and Elizabeth K Mann[1]; [1]Physics, Kent State University, Kent, Ohio; [2]Mathematics, Harvey Mudd College, Claremont, California; [3]Mathematics, Case Western Reserve University, Cleveland, Ohio; [4]Chemical Engineering, Case Western Reserve University, Cleveland, Ohio.

We present a new, simplified model of the dynamics of molecular layers on a fluid substrate. This is used to deduce the line tension of 8CB multilayers confined at the air/water interface from the relaxation of elongated domains towards circles, driven by line energy minimization. The model allows us to consider a range of initial states, beyond the slightly deformed states previously considered. 8CB, a smectic liquid crystal in bulk, forms multiple, interdigitated layers at the water surface. Domains of different thickness coexist, separated by microscopic boundaries. Previous work [1] estimated the line tension for the thinnest two layers and found a factor of 10 difference. We extend these results to as many as 10 multilayers, which allows us to consider mechanisms for the line energy. [1] J. Langer, C.R. Robertson, C. W. Frank, G. G. Fuller, Langmuir, 12: 5630 (1996).

P7.35
Dynamics of membranes with polymers having equally spaced anchors confined within the bilayers. Jyotsana Lal[1], Xuesong Hu[1], Ralf Biehl[2], Michael Monkenbusch[2] and Robert K. Prud'homme[3]; [1]Argonne National Labs., Intense Pulsed Neutron Source, Argonne, Illinois; [2]Institut fur Festkorperforschung, Forschungszentrum, Julich GmbH, D-52425 Julich, Germany; [3]Dept. of Chemical Engineering, Princeton University, Princeton, New Jersey.

Membrane undulations of highly ordered bare nonionic surfactant penta(ethyleneglycol) dodecy ether (C12E5) multilayers were studied by Neutron Spin Echo Spectroscopy (NSE). The membrane relaxations profiles were fitted by a stretched exponential law $S(q,t)=S(q)\ \exp(Gq\ t)\hat{3}/2$ where S(q) is the static structure factor and Gq is the relaxation rate. The universal scaling law Gq $\sim q\hat{3}$ for qd $>$ 1, where d is the inter-lamellar spacing was observed. From the dependence of Gq on d as obtained for different surfactant volume fractions , shows that intermembrane contributions are still important at these q values. A model comb-graft polymer with monodisperse Polyethylene glycol (PEG) blocks of 6kg/mol connecting C18 stearylamide hydrophobes, which serve as anchors, was introduced in the lamellar phase at increasing polymer concentration at two membrane volume fraction of 20 and 30%.

P7.36
The effect (or lack thereof) of water on friction and adhesion for diamond-like carbon films. Erin E. Flater[1], Kumar Sridharan[2,1] and Robert W Carpick[1]; [1]Engineering Physics, University of Wisconsin - Madison, Madison, Wisconsin; [2]Center for Plasma Aided Manufacturing, University of Wisconsin - Madison, Madison, Wisconsin.

Diamond-like carbon (DLC) films have been used many years for a range of tribological applications, mainly due to their low intrinsic

friction as well as relatively high stiffness and hardness. However, it is almost universally observed that this material's superior frictional performance occurs only at low relative humidity (RH). In the present study, we seek to understand more fully the fundamental relations that govern the tribology of DLC at the nanoscale, and particularly how humidity tends to reduce the superior frictional properties of DLC. Atomically smooth coatings of DLC were deposited on silicon substrates using a process known as plasma source ion deposition. Friction and adhesion between DLC and silicon nitride probe tips were measured using atomic force microscopy. At low loads, friction increases with increasing RH while the adhesion remains absolutely constant. Furthermore, the friction varies with load in excellent agreement with the Derjaguin-Muller-Toporov theory of adhesive elastic contacts. This indicates that the increased friction force is not due to an increased contact area facilitated by enhanced adhesive bonding in the presence of either water molecules or a water meniscus. Rather, the results can only be explained by an intrinsically stronger interfacial shear strength. We will discuss how these results affect the interpretation of the macroscopic friction performance of DLC. This work was supported by the US Department of Energy, BES-Materials Sciences, under Contract DE-FG02-02ER46016.

P7.37
Reorientation and Diffusion of Single Molecules in Thin Polymer Films. Frank Cichos, Arne Schob, Joerg Schuster and Christian von Borczyskowski; Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany.

The rotation-translation paradoxon is one of the complex phenomena observed close to the glass transition. In the region between T_g and $1.2T_g$ rotation and translation do not show the same viscosity dependence. While rotational diffusion follows the Stokes-Einstein-Debye scaling with $\tau_{rot} \sim \eta$, translational diffusion shows a different scaling with viscosity ($\tau_{trans} \sim \eta^{\alpha}$, $\alpha<1$). This effect is supposed to origin from a coupling of rotational and translational motion. To explore this paradoxon we study the rotational and translational diffusion of single dye molecules in thin polymer films of PMA at temperatures above the glass transition (T_g=281K). We use a wide field fluorescence microscopy setup to image the orientation and position of individual dye molecules. The experiments show that the rotational motion of individual dye molecules is heterogeneous. The molecules undergo sudden changes in the rotational time constant, which means that they are traveling through a space of different physical properties of the polymer at constant temperature. A time constant for this environmental exchange is defined which is found to be one order of magnitude larger than the one characterizing the rotational motion. At temperatures of 69K (1.2 T_g) above the glass transition translational motion becomes clearly detectable. However, despite the dynamical heterogeneity in rotational motion no anomalous diffusion is found for the translation. The mean square displacement of single molecule trajectories shows a linear behavior. The step size distribution of the diffusion process is clearly Gaussian. This means that the dynamical processes causing the heterogeneity in the rotation have become to fast to be influence the translational diffusion on the timescale of our experiment.

P7.38
Single Molecule Dynamics in Confined Liquids. Arne Schob[1], Frank Cichos[1] and Regine von Klitzing[2]; [1]Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany; [2]Stranski-Laboratory, Sekr. ER1, Technical University Berlin, Berlin, Germany.

The confinement of liquids leads to new effects which are induced by the interaction of the liquid with the surface. A tool to study such effects is i.e. the surface forces apparatus, which has shown, that i.e. the viscosity of some liquids is enhanced due to the confinement. Further, the interaction at the liquid-solid interface leads to an ordering effect which gives rise to an oscillating density profile perpendicular to the surface known as liquid layering. This periodic density enhancement decays exponentially with increasing distance from the surface. Therefore liquid density as well as viscosity enhancement should not be constant over the confining gap. The details of this heterogeneity are the subject of our single molecule studies, from which we present first efforts in this contribution. We have coupled a wide field fluorescence microscope to a home built surface forces apparatus. We are thus able to track single fluorescent molecules in confined liquid films of variable thickness. First experiments indeed show an enhancement of the fluorescence upon confinement and a rather broad distribution of molecular diffusion coefficients. In a second experiment the solid surfaces are replaced by the vapor phase in which we stabilize a freely standing liquid films of polyelectrolytes. In a similar way such polyelectrolytes show a near ordering in thin films of a few ten nanometer thickness. The length scale of this near order however corresponds rather to a network mesh dimension rather than to a molecular size. Thus the ordering is of different origin and specially the transport mechanisms involved in the thinning of the film are of interest. In the same manner video microscopy on dye labeled polyelectrolyte molecules in freely standing polyelectrolyte films is carried out to understand the transport mechanisms during the layering transitions. The poster will summarize the current results of the experiments.

P7.39
A Dynamical Model of Molecular Monolayers: Why Tethers Don't Snap. Andrew J Bernoff[1], James C Alexander[2], J. Adin Mann[3] and Elizabeth K Mann[4]; [1]Mathematics, Harvey Mudd College, Claremont, California; [2]Mathematics, Case Western Reserve University, Cleveland, Ohio; [3]Chemical Engineering, Case Western Reserve University, Cleveland, Ohio; [4]Physics, Kent State University, Kent, Ohio.

A bola-shaped domain in a Langmuir monolayer at the air/water interface relaxes towards a circular shape under the influence of line tension. The "tether" between the two rounded ends thickens continuously in this process, in marked contrast to the Hele-Shaw and the three-dimensional cases, where hydrodynamic instabilities lead to the tether snapping. A simplified dynamical model allows us use lubrication theory to explain this behavior without incorporating repulsive forces to stabilize the tether in 2D. The model also allows us to give a better estimate of line tensions from the relaxation rate of such monolayer domains.

P7.40
Bent-core Liquid Crystals at the Air/Water Interface. Ji Wang[1], Lu Zou[1], Violeta J Beleva[1], Edgar E. Kooijman[1], Antal Jakli[2] and Elizabeth K Mann[1]; [1]Physics, Kent State University, Kent, Ohio; [2]Liquid Crystal Institue, Kent State University, Kent, Ohio.

A series of bent-core, or bow-shaped, liquid crystals were spread at the air/water interface, and their behavior studied through surface pressure isotherms and Brewster angle microscopy. Because of the bow shape, many different configurations of the molecules with respect to the surface are imaginable. A subset of these is explored as the available surface area decreases. The behavior observed depends strongly on the groups making up the sidechains to the liquid crystals and on substitutions on the phenol rings making up the core of the molecule. To our knowledge, this work is the first systematic study of the monolayer behavior of a series of such bow shaped molecules. The variety of structures at the surface should allow us to form Langmuir-Blodgett layers serving as alignment layers with very different pre-tilt angles.

P7.41
Molecular Conformation and Dynamics in Ultrathin Polymer Films. Svetlana V Primak, Lu Zou and Elizabeth K Mann; Physics, Kent State University, Kent, Ohio.

The ability of polydimethylsiloxane (PDMS) to coat surfaces to modify their properties leads to the utilization of PDMS and its derivatives in everything from cosmetics to release agents. Information on structural mechanisms for macromolecular packing and dynamics in the ultrathin film remains lacking. We use deuterium nuclear magnetic resonance (DNMR) to probe for methyl side-group ordering induced by the surface, which also gives insight into backbone conformation. Anopore membranes provided enough well-oriented surface for PDMS film deposition to obtain good DNMR signals for layers with average thickness between 0.2 and 10 nm. Studies at room temperature and below the surface glass transition for the polymer provide complementary results.

P7.42
Relaxation kinetics in two-dimensional structures. Jose L. Iguain and Laurent J. Lewis; Departement de Physique, Universite de Montreal, Montreal, Quebec, Canada.

We have studied the approach to equilibrium of islands and pores in two dimensions. The two-regime scenario observed when islands evolve according to a set of particular rules, namely relaxation by steps at low temperature and smooth at high temperature, is generalized to a wide class of kinetic models and the two kinds of structures. Scaling laws for equilibration times are analytically derived and confirmed by kinetic Monte Carlo simulations.

P7.43
Dynamics of Buried Polymer -polymer Interfaces in Thin Films. Laurence Bruce Lurio[1], Xuesong Hu[2], Suresh Narayanan[3], Xuesong Jiao[1] and Jyotsana Lal[2]; [1]Department of Physics, Northern Illinois University, Dekalb, Illinois; [2]IPNS, Argonne National Laboratory, Argonne, Illinois; [3]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

X-ray photon correlation spectroscopy (XPCS) can be used to probe the dynamics at a glassy liquid surface over microscopic lengths

(~50-5000 nm)[1,2]. For polymer films this technique is particularly interesting, since deviations from bulk behavior may occur for diffusive motion over length scales comparable to Rg. We have developed a new technique to measure XPCS from a supported polymer bi-layer. The bi-layer is chosen so that the critical angle for total external reflection for the top layer is smaller than that for the bottom layer. When x-rays are incident below the critical angle of the top layer only the structure and dynamics of the top layer are probed. When x-rays are incident above the critical angle of the top layer but below that of the bottom layer, a standing wave is set up. The phase of this standing wave can be adjusted to have a maximum at the polymer-polymer interface and simultaneously a node at the polymer-air interface. Consequently one can isolate the static scattering and XPCS from the buried layer. Results on a system consisting of a 100 nm polystyrene film on top of an 80 nm polybromostyrene film, supported on a Si substrate will be discussed. This work was supported by NSF Grant DMR-0209542 and DOE grants DE-FG02-96ER45593 and W-31-109-ENG-38. 1Kim, H., A. Ruhm, L. B. Lurio, J. K. Basu, J. Lal, D. Lumma, S. G. J. Mochrie, and S. K. Sinha, PRL, 90, 2003, 068302. 2Seydel, T., A. Madsen, M. Tolan, G. Grubel, and W. Press, 2001, PRB, 63, 2003, 073409.

P7.44
From Rolling Ball to Complete Wetting on Dynamically Tunable Nanostructured Surfaces. Tom N Krupenkin[1], Ashley Taylor[2], Tobias M Schneider[1] and Shu Yang[1]; [1]Bell Labs, Lucent Tech., Murray Hill, New Jersey; [2]New Jersey Nanotechnology Consortium, Murray Hill, New Jersey.

An ability to manipulate microscopic volumes of liquids with the high precision becomes increasingly important with the recent progress in micro- and nanofluidics and its rapid penetration in various industrial applications. Dynamic control over the interaction of liquids with the solid substrate constitutes a very important aspect of this problem. Nanostructured solid surfaces offer a promising way to achieve this goal. In this talk we discuss a successful demonstration of dynamically tunable nanostructured surfaces. The state of liquid droplets on these surfaces can be dynamically changed all the way from the superhydrophobic rolling ball sate to almost complete wetting by the application of a small voltage, as well as by several other means. The proposed approach potentially allows novel methods of manipulating microscopically small volumes of liquids. This includes almost frictionless liquid transport, the ability to selectively immobilize the droplets at any given time or position, self-assembly of liquid drops, as well as dynamic control over the penetration on liquids through the nanostructured layer. The obtained results potentially open new and exciting opportunities in microfluidics, optics, thermal management of microelectronics, chemical microreactors, bio/chemical detection, and many other areas.

P7.45
Abstract Withdrawn

P7.46
Detection of Interfacial Structures of Poly(ethylene glycol), Poly(propylene glycol) and Their Copolymers at Liquid/Solid Interfaces Using Sum Frequency Generation Vibrational Spectroscopy. Chunyan Chen, Jie Wang, Mark A Even and Zhan Chen; Chemistry, University of Michigan, Ann Arbor, Michigan.

Molecular structures of liquids at interfaces are very different from those in the liquid bulk. Studies on liquid polyethers such as poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), and especially their copolymer PEG-PPG-PEG (known as pluronics) at different interfaces have been of great interest for decades due to their broad applications. We have applied sum frequency generation (SFG) vibrational spectroscopy, a submonolayer surface sensitive analytical technique, to study interfacial structures of PEG, PPG, their solutions, their copolymers, and copolymer solutions while contacting different media including air, fused silica, and various polymers. For the first time, conformations of polyether materials at various interfaces have been shown at the molecular level in situ. Depending on the hydrophobicity of the solid contacting media, the liquid polymers PEG and PPG show different conformations at different interfaces, which can be correlated to molecular interactions at these interfaces. The favorable interaction between hydrophobic media and the hydrophobic segments, methylene or methyl groups, of polyethers causes an ordered conformation with these groups standing up at the interface. The unfavorable interaction between hydrophilic media and hydrophobic segments of the polyethers induces interfacial methylene or methyl groups to have a random structure or to lie down at the interfaces, indicated by the weakening or even absence of SFG signals. For comparison, interfaces between aqueous PEG or PPG solutions and air, polystyrene, poly(methyl methacrylate), and fused silica have also been investigated. In addition, we have studied conformations of pluronics at various interfaces, showing that different blocks have different interface activities. The interfaces are always dominated by the PPG segments. The studies on molecular level interfacial structures of PEG, PPG and pluronics will help us to understand and control the interfacial behavior of liquids at interfaces.

P7.47
Dynamics of Xenon gas adsorbed inside of Single-walled carbon nanotubes studied by 129Xe-NMR. Hironori Ogata[1] and Yahachi Saito[2]; [1]Materials Chemistry, Hosei University, Tokyo, Japan; [2]Electronics and Electronic Engineering, Mie University, Tsu, Japan.

It is well known that 129Xe-NMR of Xenon gas adsorbed in confined pore is essential way to investigate the pore structure. 129Xe-NMR for Xenon gas adsorbed SWNTs were studied. At room temperature, the 129Xe-NMR spectrum for Xenon gas adsorbed SWNT sample after heat treatment shows the weak broad peak around 120-130 ppm from that of free Xenon gas extrapolated at zero pressure. From the pressure dependence of Xenon gas on the peak position, this peak is assigned to be attribute to the Xenon gas confined inside the tube space. From the temperature dependence of 129Xe-NMR, dynamics ofconfined Xenon gas will be discussed.

P7.48
Abstract Withdrawn

SESSION P8:
Chair: Rainer Kimmich
Thursday Morning, December 4, 2003
Room 309 (Hynes)

8:30 AM *P8.1
Adsorption and Diffusion in Highly Disordered Microporous Carbons: Molecular Simulation vs. Experiment. Jorge Pikunic[1], Roland Pellenq[2], Pierre Levitz[3] and Keith E. Gubbins[1]; [1]Chemical Engineering, North Carolina State University, Raleigh, North Carolina; [2]Centre de Recherche sur les Mecanismes de la Croissance Cristalline, CNRS, Marseille, France; [3]Laboratoire de Physique de la Matiere Condensee, Ecole Polytechnique, Palaisau, France.

We present molecular simulation results for adsorption and diffusion of simple fluids in realistic models of microporous carbons. The model carbons are contstructed using a constrained reverse Monte Carlo method that quantitatively matches the experimental diffraction data of real microporous carbons. In the reverse Monte Carlo procedure, we use carefully selected constraints that describe the three-body correlations. Through successive Monte Carlo moves, using a simulated annealing scheme, the model structure is matched to the experimental diffraction data (X-ray diffraction and Small Angle X-ray Scattering) subject to the imposed three-body constraints. A series of saccharose-based carbons are modeled, and the models are tested against high resolution transmission electron microscopy (TEM) data. Simulated TEM images of the resulting structural models are in very good agreement with experimental ones. For the carbons studied, the pore structure is highly convoluted, and the commonly used slit pore model is not appropriate. We simulated argon adsorption and xenon diffusion in the resulting models using grand canonical Monte Carlo and canonical molecular dynamics simulations, respectively. The simulation results are compared with adsorption, calorimetry, and NMR measurements. The simulated adsorption isotherms, heats of adsorption, and self-diffusivities show the same behavior as that observed experimentally. Similar calculations for slit pores with the same pore size distribution show different qualitative behavior from the experiments.

9:00 AM *P8.2
Nucleation of Bubbles and Droplets in Confined Fluids. Alexander V Neimark, Aleksey Vishnyakov and Peter Ravikovitch; TRI/Princeton, Princeton, New Jersey.

We present new MC simulation methods developed to monitor the formation of nuclei in metastable nanophases and to calculate the nucleation barriers. The methods are illustrated on three classical systems: formation and snap-off of liquid bridges in cylindrical capillaries, cavitation of a bubble in a supersaturated vapor confined in a spherical cavity with repulsive walls, and nucleation of a droplet in a strechted metastable liquid confined in a spherical cavity with attractive walls. The simulation results are compared with the non-local density functional theory and the capillary condensation - evaporation experiments on regular nanoporous materials.

9:30 AM P8.3
Seminal, Direct Measurement of the Distribution of Glass Transition Temperatures in Nanoscopically Confined Glass Formers: Novel Fluorescence Studies. Christopher J. Ellison and John M. Torkelson; Dept. of Chemical Eng. & Dept. of Materials Science and Eng., Northwestern University, Evanston, Illinois.

Despite the decade-long study of the effect of nanoconfinement on the glass transition temperature, Tg, of amorphous materials, the quest to probe the distribution of Tgs in nanoconfined glass formers has remained unfulfilled. Here the distribution of Tgs across polystyrene (PS) and poly(vinyl pyridine) (PVP) films has been obtained by a novel, fluorescence label /multilayer method. The temperature dependence of pyrene probe or label fluorescence has been shown to yield determinations of Tg in single-layer polymer films in excellent agreement with ellipsometry and reflectometry data by Jones and co-workers and Wu and co-workers. When bulk, multilayer films are constructed with one layer (as thin as 12 nm) containing pyrene label, the label fluorescence reveals that the enhancement of average cooperative dynamics (the dynamics associated witth Tg) at the free surface affects Tg several tens of nanometers into the film. In the case of PVP films which exhibit attractive interactions (hydrogen bonding) with silica substrates, the slowing of average cooperative dynamics at the substrate interface exhibits a longer range impact into the film than occurs with the free surface. The extent to which average cooperative dynamics transition from an enhanced state to bulk states across the film thickness depends strongly on nanoconfinement. When PS films are sufficiently thin that a reduction in thickness leads to a reduction in overall Tg, the surface-layer Tg actually increases with a reduction in overall thickness while the substrate-layer Tg decreases. These results indicate that the gradient in Tg dynamics across the film is not abrupt and that the size of a cooperatively rearranging region is much smaller than the distance over which interfacial Tg effects propagate. However, an indication that there may be a relationship between the size scale of a cooperatively rearranging region and the length scale over which nanoconfinment/interfacial effects propagate in ultrathin polymer films is revealed from studies on single-layer plasticized polymer films. When PS or PVP films are plasticized by substantial levels of pyrene dopant or the classic plasticizer dioctyl phthalate, the impact of nanoconfinement on Tg is either greatly reduced (relative to unplasticized films) or eliminated at least down to 20-nm thick films. As the presence of plasticizer results in a reduction of the number of segments needed to undergo cooperative motion, relative to unplasticized films the size of cooperatively rearranging regions are reduced in plasticized films. Further study of these effects is ongoing.

10:15 AM *P8.4
Structure, Dynamics and Phase diagram of molecular liquids confined in mesoporous materials.
Christiane Marie Alba-Simionesco[1], Gilberte Dosseh[1], Krystel Lequellec[1], Nancy Brodie-Linder[2], Yongde Xia[1], Bernhard Frick[3] and Georg Ehlers[3]; [1]Lab Chimie Physique, CNRS, ORSAY, France; [2]dpt chemistry, Univ Cergy Pontoise, Cergy, France; [3]ILL, Grenoble, France.

When confined within a pore with a typical size of a few molecular diameters, dynamical and static properties of a liquid are strongly affected : the phase transitions, such as melting, freezing and glass formation, depend remarkably on the pore size and on the nature of the surface. Especially for aromatic liquids such as benzene, toluene and o-terphenyl confined in a series of cylindrical mesoporous materials (MCM-41 and SBA-15 with pore diameter from 2.4 to 14 nm), when freezing is avoided under standard conditions of cooling, a glass transition is observed with a non trivial pore size dependence. Very long time dynamics in the window of the adiabatic calorimetry is compared to subnanosecond dynamics from inelastic neutron scattering (backscattering, TOF, NSE), leading to both a very heterogeneous dynamics and a slowing down and speeding up of the structural relaxation. Moreover confined geometry has generated much interest since it is a possible operational procedure for extracting information on the mesoscopic properties of the liquid from size effects: an enhanced mobility of the inner part of the liquid with respect to the bulk is reported depending on the pore size, while an interfacial layer seems highly affected by surface interactions and may present a significantly slower dynamics. One might argue that this inner part is poorly affected by surface interaction and thus invoke just size effects. Furthermore, the density of the confined fluid is obtained from the intensity of Bragg diffraction peaks of the mesoporous materials and related to the local structure of the liquids measured by elastic neutron scattering at large wave numbers, and this latter result is questioning on the relevant thermodynamic path to the glass transition followed by an experiment at 'ambient pressure' in confined geometry. Deviations from the bulk behavior and additional features occurring from the complex interplay from size and interface effects are presented and our results provide a good indications of the existence of a mesoscopic length in supercooled liquids. In addition a schematic phase diagram of confined fluids in such materials is proposed.

10:45 AM P8.5
Grand Canonical Monte-Carlo Study of Adsorption and Condensation in Nanopores:From Simple Pore geometry to Disordered Matrix.
Roland Pellenq[1] and Benoit Coasne[2]; [1]CRMC2-CNRS, Marseille, France; [2]Groupe de Physique des Solides, Universite Paris 6 & 7 - CNRS, Paris, France.

Argon adsorption (77 K) in silica nanopores of various sizes and shapes including a silica glass (Vycor), has been studied by Grand Canonical Monte Carlo simulations. We discuss the effects of confinement, pore morphology and surface texture on the thickness variation of the adsorbed film with pressure. The different pore geometry also allow clarifying the status of capillary condensation/evaporation [1]. Simulations in cylindrical pores open at one or both ends, validate the Cohan adsorption processes. We discuss the effect of the finite or infinite pore length on the desorption mechanism. In the case of the pore open at one end, we show that desorption is not modified by the presence of an external plane surface. We consider the effect of morphological defects on adsorption. Condensation/evaporation pressures in the ellipsoidal pore are greatly lowered compared to the case of the cylindrical pore having the same section area. Furthermore, we show that the filling mechanism is significantly affected by the presence of a constriction in a pore open at one or both ends. Desorption in the closed constricted pore shows that the evaporation of the cavity is triggered by the evaporation of the fluid in the constriction. This evaporation process conforms to the 'pore blocking effect'. Most of Vycor isotherm features are present in the constricted pore. [1] B. Coasne et al, Phys. Rev. Lett. 88, 256102 (2002).

11:00 AM *P8.6
Slow Dynamics and the Glass Transition in Confining Systems.
Ranko Richert, Chemistry and Biochemistry, Arizona State University, Tempe, Arizona.

The structural relaxation of a glass-forming liquid becomes slow at temperatures near the glass transition. In this viscous regime, the liquid is very sensitive to surface and finite size effects and a number of apparently controversial results have been reported for the dynamics in small confining systems. A more complete understanding of the behavior of liquids in nanoporous materials requires a detailed account of surface chemistry, surface curvature, surface roughness, interactions at the liquid/solid interface, isobaric versus isochoric conditions, separation of finite size and interfacial effects. We use the method of triplet state solvation dynamics in order to study the dynamics in porous glasses as a function of pore size, surface chemistry [1], and (more recently) as a function of the distance from the surface [2]. By bonding the optical probes to the pore wall, we observe interfacial dynamics which are three orders of magnitude slower compared with the bulk, equivalent to the situation of a glassy surface layer surrounding a fluid inner pore material [3]. Consistent with length scales of cooperativity, these effects disappear for distances from the surface exceeding a few nanometers. [1] C. Streck, Yu.B. Mel'nichenko, R. Richert, Phys. Rev. B 53 (1996) 5341 [2] R. Richert, M. Yang, J. Phys. Chem. B 107 (2003) 895 [3] R. Richert, M. Yang, J. Phys.: Condens. Matter 15 (2003) S1041

11:30 AM P8.7
Surface glass transition of bimodal polysytrene mixtures investigated by the embeddig of noble metal nanoclusters.
Joern Erichsen, Tesfaye Shiferaw, Ulrich Schuermann, Vladimir Zaporojtchenko and Franz Faupel; Chair for Multicomponent Materials, Christian-Albrechts University, Kiel, Germany.

The temperature dependent embedding process of noble metal nanoclusters into polymers was used to probe the surface glass transition. X-ray photoelectron spectroscopy (XPS) was applied to study the embedding of Au nanoclusters into polystyrene [1]. Previously a small decrease of glass transition temperature (Tg) at the surface compared to the bulk, which decreases at low Mw, was detected with this method [1,2]. Transmission electron microscopy (TEM) investigations yield the same cluster sizes and densities for a height and a low molecular weight. Therefore probe size effects can be excluded. In order to understand the Tg depression we present measurements on bimodal mixtures of monodisperse polystyrenes (Mw = 3.5 and 1000 kg/mol). The results on the bimodal mixtures rule out the interpretation that the Tg depression at the surface is due to an enrichement of shorter chains. [1] V. Zaporojtchenko, T. Strunskus, J. Erichsen, F. Faupel, Macromolecules, 34(5) (2001) 1125. [2] J. Erichsen, K. Guenther-Schade, K. Dolgner, V. Zaporojtchenko, T. Strunskus, and F. Faupel, Mat. Res. Soc. Symp. Proc. Vol. 710 (2002).

SESSION P9:
Chair: Gleb Oshanin
Thursday Afternoon, December 4, 2003
Room 309 (Hynes)

1:30 PM *P9.1
Probing into Transport of Fluids in Porous Media on Length

Scales from Millimeters to Nanometers by NMR.
Rainer Kimmich[1], Elmar Fischer[1], Markus Weber[1], Elke Kossel[1] and Uwe Beginn[2]; [1]Sektion Kernresonanzspektroskopie, University of Ulm, Ulm, Germany; [2]ITMC/Tex MC, RWTH, Aachen, Germany.

Confinement effects on hydrodynamic flow and electric current on the one hand and self-diffusion on the other were studied in porous media as coherent and incoherent transport mechanisms, respectively. Coherent transport pathways are visualized with the aid of magnetic resonance microscopy techniques. The physical origins of diffusion anomalies are elucidated. We use the well-known reptation model theory for the determination of pore diameters on a nanometer length scale. The electric current density in percolation clusters was mapped with the aid of an NMR microscopy technique monitoring the spatial distribution of spin precession phase shifts caused by the currents [1,2]. A test structure and quasi two-dimensional random-site percolation model objects filled with an electrolyte solution were examined and compared with numerical calculations based on potential theory. The current density maps permit the evaluation of histograms and of volume-averaged current densities as a function of the probe volume radius as relationships characterizing transport in the clusters. The current density maps are juxtaposed to velocity maps acquired in flow NMR experiments in the same objects. It is demonstrated that electric current and hydrodynamic flow lead to transport patterns deviating in a characteristic way from each other due to the different dependences of the transport resistances on the pore channel width [2]. Diffusion of linear polymers in pores of a solid matrix is sensitive to the diameter of the confinement on a much shorter length scale [3]. Based on the reptation model theory it is shown that the pore diameter can directly be evaluated from echo attenuation curves provided that the appropriate evaluation formalism is employed [4]. With a series of samples prepared for this purpose, pore dimensions between 6 and 80 nm were determined in agreement with data from other techniques. [1] G. C. Scott, M. L. G. Joy, R. L. Armstrong, and R. M. Henkelman, J. Magn. Reson. 97, 235 (1992). [2] M. Weber, R. Kimmich, Phys. Rev. E 66, 026306 (2002). [3] A. Denissov, M. Kroutieva, N. Fatkullin, R. Kimmich, J. Chem. Phys. 116, 5217 (2002). [4] R. Kimmich, N. Fatkullin, Advances in Polymer Science, 2003, in press.

2:00 PM *P9.2
Influence of Confinement on Polymer-Electrolyte Relaxational Dynamics. Jean-Marc Zanotti[1,2], Luis J. Smith[3], Michel Armand[4], Pierre Levitz[5], David L. Price[6,1] and Marie-Louise Saboungi[7]; [1]Intense Pulsed Neutron Source, Argonne Nat. Lab., Argonne, Illinois; [2]Laboratoire Leon Brillouin, CEA-CNRS, Gif-sur-Yvette, France; [3]Material Science Division, Argonne Nat. Lab., Argonne, Illinois; [4]UMR Internationale CNRS 2289, Montreal University, Montreal, Quebec, Canada; [5]LPMC, CNRS-Ecole Polytechnique, Palaiseau, France; [6]CRMHT, CNRS-Universite d Orleans, Orleans, France; [7]CRMD, CNRS-Universite d Orleans, Orleans, France.

Conception and industrial production of viable high specific energy/power batteries is a central issue for the development of non-polluting vehicles (EV & HEVs). In terms of stored energy and safety, solid-state devices using polymer electrolytes are highly desirable. One of the most studied systems is PEO (polyethylene oxide) complexed by Li salts. Polymer segmental motions and ionic conductivity are closely related [1]. Bulk PEO is actually a biphasic system where an amorphous and a crystalline state (Tmelting=335 K) coexist. To improve ionic conduction in those systems requires a significant increase of the amorphous phase fraction where lithium conduction is known to mainly take place. As far as ionic conduction is concerned, operation above 80oC is satisfactory but this requirements limits consumer use to niche applications. Confinement strongly affects properties of condensed matter and in particular the collective phenomena inducing crystallization. Confinement of the polymer matrix is therefore a possible alternative route to the unpractical use of high temperature. Results of a quasi-elastic incoherent neutron scattering study of the influence of confinement on polyethylene oxide (PEO) and (PEO)8Li+[(CF3SO2)2N]- (or (POE)8LiTFSI) dynamics are presented. The nano-confining media is Vycor, a silica based hydrophilic porous glass (characteristic size of the 3D pore network = 50 Å). As supported by DSC measurements, the PEO melting transition at 335 K is strongly attenuated under confinement, suggesting that space delimitation modifies the global structure of the system, increasing the fraction of amorphous PEO by respect to crystalline phase. As expected, the presence of Li salt slows down the bulk polymer dynamics. The confinement also affects dramatically the apparent mean-square displacement of the polymer. Local relaxational PEO dynamics is successfully described by a generalized DLM (Dejean-Lauprêtre-Monnerie) model [2] usually used to interpret NMR spin-lattice relaxation time data. The scattering vector dependence of the correlation times deduced from inelastic neutron scattering data is found to obey a power-law dependence. [1] J. P. Donoso et al., J. Chem. Phys. 98 10026, (1993) [2] R. Dejean de la Batie, F. Lauprêtre and L. Monnerie, Macromolecules, 21, 2045 (1988). This work was supported by the Office of Science, US Department of Energy, under Contract W-31-109-ENG-38, by Commissariat à l' Energie Atomique (CEA, France) and Centre National de la Recherche Scientifique (CNRS, France).

2:30 PM P9.3
Polymers In Random Nanoporous Glasses: Molecular Dynamics And Structure. Andreas Schoenhals[1], Harald Goering[1], Christoph Schick[2], Bernhard Frick[3] and Reiner Zorn[4]; [1]VI.3, Federal Institute of Materials Reserach and Testing, Berlin, Germany; [2]Department of Physiscs, University Rostock, Rostock, Germany; [3]Institute Laue - Langevine, Grenoble, France; [4]Institute for Solid Sate Research, Juelich, Germany.

The molecular dynamics of poly(propylene glycol) (PPG) and poly(dimethyl siloxane) (PDMS) confined to nanoporous glasses revealed by dielectric spectroscopy (DS), temperature modulated DSC (TMDSC) and neutron scattering (NS) are compared. For both systems the relaxation rates estimated by DS and TMDSC agree quantitatively indicating that both experiments sense the glass transition. For PPG the segmental dynamics is determined by a counterbalance of adsorption and confinement effect. The former results from an interaction of the macromolecules with the internal surfaces. A confinement effect originates from a length scale on which the molecular motions takes place. The increment of the specific heat capacity Dcp at the glass transition vanishes at a length scale of 1.8 nm. Both results support the conception that a characteristic length scale is relevant for glassy dynamics. For PDMS only a confinement effect is observed which is stronger than that for PPG. Down to a pore size of 7.5 nm the temperature dependence of the relaxation times follows the Vogel-Fulcher-Tammann dependence. At a pore size of 5 nm this changes to an Arrhenius-like behaviour. At the same pore size Dcp vanishes for PDMS. NS experiments reveal that the diffusive character of the molecular motions - found to be characteristic above Tg- seems to disappear at this length scale. These results give support that the glass transition has to be characterised by a length scale of the relevant molecular motions.

3:15 PM P9.4
Existence and Effects of Enhanced Surface Mobility of Polymer Films. James Forrest[1], James Sharp[2,1] and Jonathan Teichroeb[1]; [1]Physics, University of Waterloo, Waterloo, Ontario, Canada; [2]Physics and Astronomy, University of Nottingham, Nottingham, United Kingdom.

We have performed a detailed study on the properties of the free surfaces of thin polystyrene films, and the effect the free surface has on the glass transition temperature Tg. In the first case we directly probe the viscoelastic properties of the free surface by using Atomic Force Microscopy (AFM) to monitor the embedding of gold nanospheres into polystyrene (PS) films. For 20 nm nanospheres, we find that the embedding occurs at temperatures as low as 10K below the bulk glass transition temperature. The embedding takes place over a time period of ~100 minutes and for all temperatures T < Tg, reaches a depth of 3-4 nm. Experiments using 10 nm spheres also show embedding to a depth of 3-4 nm over a similar time period. These observations suggest that the embedding for T < Tg is not a yield process in a glassy polymer, but rather due to the existence of a surface layer of size 3-4 nm with instrinsically faster dynamics. In order to determine if this more mobile layer is directly related to lower Tg values observed in thin PS films, we made films where the free surface was covered. In PS films where the free surface was covered with an evaporated Au layer, no Tg reductions were observed. For films coated with Al, we are able to show that by applying a more elaborate sample preparation procedure (where we do not evaporate directly onto the PS films) PS films show no Tg reductions even for films as thin as 8 nm. These Tg measurements show that removing the free surface eliminates Tg reductions in thin PS films. The combined results of the nanosphere embedding and Tg measurements strongly suggests that the free surface has higher mobility than the bulk polymer, and that this is a key contributing factor to Tg reduction in thin PS films.

3:30 PM P9.5
Inelastic neutron scattering studies on glass forming systems in confinement. Bernhard Frick[1], Christiane Alba-Simionesco[4], Spiros Anastasiadis[7], Kiriaki Chrissopoulou[7], Kari Dalnoki-Veress[5], Gilberte Dosseh[4], James Forrest[8], Lutz Hartmann[10], Christelle Lequellec[4], Angel Moreno[9,6], Andreas Schoenhals[2] and Reiner Zorn[3]; [1]Institut Laue-Langevin, Grenoble, France; [2]BAM, Berlin, Germany; [3]IFF, Juelich, Germany; [4]LCP, CNRS, Orsay, France; [5]McMaster University, Hamilton, Ontario, Canada; [6]UPV/EHU, San Sebastian, Spain; [7]Foundation for Research & Technology - Hellas and Univ. of Crete, Heraklion, Greece; [8]University of Waterloo, Waterloo, Ontario, Canada; [9]LDV, Universite de Montpellier, Montpellier, France; [10]Universitaet Leipzig, Leipzig, Germany.

Due to its high penetration power inelastic neutron scattering is an ideal tool for the investigation of the dynamics of confined fluids and glasses on a time scale of nano- to picoseconds with simultaneous spatial resolution. We review recent experimental investigations at the time-of-flight (TOF) and backscattering (BS) instruments of the Institut Laue-Langevin on different glass forming systems among which are the low molecular glass formers toluene, salol, ortho-terphenyl (OTP), and polymers as polydimethylsiloxane (PDMS), polymethylphenylsiloxane (PMPS) and polystyrene (PS). These systems were confined in matrices like MCM-41, controlled pore glasses (CPG) or SBA-15, with and without surface treatment of the pores. 2D- versus 3D-confinement was probed by comparing PMPS in nanocomposite clays with PMPS in CPG of pore size 2.5, 5.0 and 7.5 nm. First experiments on the dynamics of freely standing polystyrene films were also attempted. In all cases a comparison with the bulk dynamics was made. We will show that inelastic neutron scattering renders valuable information on the influence of confinement onto the local dynamics. We report on studies of the quantum tunneling of methyl groups in confinement (toluene-h3; Moreno et al.) employing the BS instrument IN16. On the same instrument we explore the change of the mean squared displacement (msd) as a function of pore size and temperature (2K-400K) for toluene-d3 and OTP (Alba-Simionesco et al.), for PDMS and PMPS (Schoenhals et al.), for different concentration of PMPS in nanocomposites (Anastasiadis et al.) and for different film thickness (50nm and 102 nm) for the free standing PS-films (Dalnoki-Veress et al.). In all cases the msd changes are discussed in relation to a possible characteristic length and a change in Tg, respectively. For several samples we were able to study the quasielastic scattering on BS and TOF and its dependence on the confinement size. The influence of spatial confinement onto the Boson peak was explored by TOF for salol, PDMS and PMPS (Zorn et al.) and shows a reduction of the low frequency states with spatial restriction.

3:45 PM P9.6
Effect of Nanoscale Confinement on the Transport Properties of Supported Ultrathin Polymer Films. Lovejeet Singh, Peter J. Ludovice and Clifford Lee Henderson; School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The effect of nanoscale confinement in modifying the physical properties of polymer thin films has recently received significant attention, particularly in the area of polymer film glass transition temperature (Tg). Depending on the nature of the interaction between the polymer and the substrate, both large increases and decreases in the polymer Tg have been observed in supported confined films. Our recent work has supported the idea that polymer chain dimensions are critical in controlling the length scale over which these effects are observed, and we have also shown the dramatic impact of nanoscale confinement on the coefficient of thermal expansion of supported polymer thin films. The focus of this paper is our expanded study of other important polymer physical properties that are modified due to nanoscale thin film confinement. In particular, the influence of thin film confinement on the diffusion coefficient of small penetrant molecules in polymer films has been studied in detail and will be presented. Changes in the diffusion behavior of small molecules in polymer thin films due to confinement has implications in a variety of fields ranging from membranes to semiconductor photoresists. The influence of film thickness and molecular weight on the diffusion coefficient of water, low molecular weight organic solvents, and various acids in a series of polymers including poly(p-hydroxystyrene), substituted polynorbornenes, and PMMA has been studied using techniques such as quartz crystal microbalance (QCM) sorption experiments. It was observed that the diffusion coefficient is a strong function of film thickness and decreases drastically as film thickness is reduced below a critical thickness value. This critical thickness value is found to be a function of both the type of polymer and its molecular weight. The total equilibrium penetrant sorption is also shown to exhibit a dependence on both polymer type, film thickness, and molecular weight. The results of these experiments and the impact of such behavior on applications such as photoresist thin films will be discussed in detail.

4:00 PM P9.7
Abstract Withdrawn

4:15 PM P9.8
Anisotropic diffusion of single molecules in ultrathin liquid films. Frank Cichos, Joerg Schuster and Christian von Borczyskowski; Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany.

Single molecule microscopy techniques deliver a tool to study dynamics on a nanoscopic scale with the advantage of resolving distributions of observables rather than mean values. Therefore it is possible to study directly heterogeneity, which is present in many systems. In our contribution we will report on experiments with single molecules in ultrathin liquid films on solids, which are intended to reveal details of the dynamics at the liquid-solid interface. We apply single molecule video microscopy to record the translational and rotational diffusion of single dye molecules in liquid films of a few nanometer thickness deposited on solid substrates. With the help of the recorded trajectories we are able to calculate distributions of diffusion coefficients. Our experiments show, that the translational diffusion in these films is considerably slowed down (1 order of magnitude) compared to the bulk. In addition the distribution of diffusion coefficients is broad and seems to result from a varying diffusion coefficient over the liquid film thickness. Further, the results even show signs of near order effects close to the surface which is known as liquid layering. Several distinct peaks appear in the distribution of diffusion coefficients, which we interpret in terms of diffusion in individual liquid layers. A consequence of the observation of distinct peaks is, that the exchange between different liquid layers is on a timescale of several ten to hundred milliseconds and thus unexpectedly slow. Due to this slow exchange we are for the first time able to observe individual exchange events in diffusion coefficient trajectories from single molecules which we obtain with a new analysis technique. Besides the diffusional motion of molecules we also observe adsorption/desorption events to/from the surface. We can characterize the duration of the adsorption event as well as the duration of the diffusion period between two adsorption events. While the latter is usually distributed by a power law for a bulk liquid interfacing a solid, we find an exponential distribution. The exponential distribution is a result of the small film thickness. The characteristic time of that exponential distribution is consistent with our view of slow molecular exchange between liquid layers parallel to the surface. The experiments demonstrate the potential of the single molecule approach to study dynamics in nanostructures of soft matter. As an outlook we will shortly summarize our current efforts on single molecule microscopy in a surface forces apparatus as well as on free standing liquid films.

4:30 PM P9.9
Segmental Dynamics of Polymers in 1 and 2nm Slit-Pores. Evangelos Manias and Vikram Kuppa; Materials Science & Engineering, Penn State University, University Park, Pennsylvania.

The local/segmental dynamics of polymers in intercalated geometries are probed with experimental methods, and the origins of the confinement-induced behavior are elucidated by Molecular Dynamics computer simulations. We comparatively study the behavior of poly(ethylene oxide) and polystyrene in extremely narrow (1nm and 2nm respectively) slit pores. In order to elucidate the mechanisms behind confinement-induced segmental dynamics of polymer chains, we contrast the high T_g PS -for which molecular motions are effectively arrested in the nanosecond time scales- to the lower T_g PEO. Our simulations complement previous experimental studies and provide a molecular perspective on the confined film behavior. Factors such as local density inhomogeneities and, in the case of PEO, the nature of lithium ion coordination, have been traced as the main molecular mechanisms responsible for the confinement-induced local segmental dynamics. In concert with previous NMR studies, we observe a very wide distribution of segmental relaxation times for the confined polymers over a broad temperature range.

4:45 PM P9.10
Molecular Level Studies on Structures and Dynamics of Moving Interfaces during Diffusion Using a Nonlinear Optical Laser Technique. Chunyan Chen, Cheryl L Loch and Zhan Chen; Chemistry, University of Michigan, Ann Arbor, Michigan.

A new nonlinear optical method, sum frequency generation (SFG) vibrational spectroscopy, has been applied to study the molecular structures of polymer/silane interfaces during diffusion of the silane into the polymer. SFG is a powerful and versatile, in situ, and submonolayer sensitive surface/interface-specific probe. The technique not only permits the identification of surface/interface molecular species, but also provides information about the surface/interface chemical structure, such as the coverage and orientation of surface/interface functional groups. The diffusion of small molecules through polymer materials plays a crucial role in many applications such as polymer coatings, membrane separations, polymer solvation and adhesion. For decades, many techniques have been extensively used to investigate such diffusion processes. However, the molecular level structure of the polymer/penetrate interface during diffusion has never been detected. Using SFG, we studied the molecular structures at the poly(methyl methacrylate) (PMMA)/N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AATM, NH2(CH2)2NH(CH2)3Si(OCH3)3) interface when the silane diffused into the polymer. Our SFG studies demonstrate that it is feasible to monitor interfacial structures at the diffused polymer/silane interface and to then evaluate the polymer/silane diffusion kinetics. We have detected that the molecular order of the polymer/silane interface exists during the whole diffusion process and is lost when the silane

molecules diffuse through the entire polymer film. We are able to detect molecular structures of these moving interfaces by collecting the SFG signals as a function of time at various IR frequencies and then constructing the time-dependent SFG spectra. By comparing the interfacial structures and the order-disorder structural transition kinetics between the polymer film and different penetrates, more detailed information about polymer/penetrate interactions can be obtained. Further SFG studies on polymer/penetrate interfaces may provide important perspectives for the design of many extensively used materials such as silane adhesion promoters, polymer membranes for separations, and polymer films used for barriers.