

**SYMPOSIUM T**  
**Dynamics in Small Confining Systems VI**

November 27 – 30, 2000

**Chairs**

**J. M. Drake**

Exxon Research and Engineering Co  
Annandale, NJ 08801  
908-730-2848

**J. Klafter**

School of Chemistry  
Tel Aviv Univ  
Tel Aviv, 69978 ISRAEL  
972-3-6408254

**Pierre E. Levitz**

CRMD  
CNRS  
1b Rue de la Ferrollerie  
Orleans, 45071 FRANCE  
33-2-38255365

**Rene Overney**

Dept Chemical Engr  
Univ of Washington  
Seattle, WA 98195  
206-543-2250

**Michael Urbakh**

School of Chemistry  
Tel Aviv Univ  
Tel Aviv, 69978 ISRAEL  
972-3-6408324

---

**Symposium Support**

ExxonMobil  
‡MMR Technologies, Inc.  
2000 Fall Exhibitor

**Proceedings published as Volume 651  
of the Materials Research Society  
Symposium Proceedings Series.**

\* Invited paper

SESSION T1:  
Chair: J. Klafter  
Monday Morning, November 27, 2000  
Room 313 (Hynes)

**8:30 AM \*T1.1**

**GLASS TRANSITIONS IN THIN POLYMER FILMS.**

Pierre Gilles de Gennes, College de France, Paris, FRANCE.

Freely standing polystyrene films show an anomalous drop of the glass temperature  $T_g$  when the molecular weight is high and the thickness smaller than the coil size  $R_0$ ; We present here a tentative explanation for these features, where two types of motions compete a) standard motions, controlled by the free volume, and independent of chain length b) collective motions along the chain, which require a weaker free volume (except for the end groups). For bulk systems, the standard motion always wins because of the end group hindrance. But for film thinner than the coil size, the dominant process may be the collective motion of a "loop" which does not involve the chain ends. What matters then is not the overall polymerisation index ( $N$ ), but the length  $g$  of a typical loop starting from the surface (which is more fluid region) and reaching deep into the film. With these ingredients, some surprising aspects of  $T_g$  ( $h, N$ ) may possibly be understood.

**9:00 AM \*T1.2**

**ANOMALOUS DIFFUSION IN ACTIVE INTRACELLULAR TRANSPORT.** Avi Caspi, Rony Granek, Michael Elbaum, Weizmann Institute of Science, Dept of Materials and Interfaces, Rehovot, ISRAEL.

The dynamic movements of tracer particles have been used to characterize their local environment in dilute networks of microtubules, and within living cells. In the former case, 300 nm diameter beads are fixed to individual microtubules, so that the movements of the bead reveal undulatory modes of the polymer. The mean square displacement shows a scaling of  $t^{3/4}$ , in keeping with mode analysis arguments. Inside a cell, beads show a more complicated behavior that reflects internal dynamics of the cytoskeleton and associated motors. When placed near the cell edge, 3 micron diameter beads coated by proteins that mediate membrane adhesion are engulfed underneath the membrane and drawn toward the center by a contracting flow of actin. On reaching the region surrounding the nucleus, the beads continue to move but lose directionality, so that they wander within a restricted space. Measurement of the mean square displacement now shows a scaling of  $t^{3/2}$  up to times of  $\sim 1$  sec. At longer times the scaling varies between  $t^1$  and  $t^{1/2}$  in the various runs. The data do not fit a crossover between ballistic ( $t^2$ ) and diffusive ( $t$ ) behavior. The movement is clearly driven by non-thermal interactions, as it cannot be stopped by an optical trap. Treatment of the cell to depolymerize microtubules restores ordinary diffusion, while actin depolymerization has no effect, indicating that microtubule-based motor proteins are responsible for the motion. Immunofluorescence microscopy shows that the mesh size of the microtubules is smaller than the bead diameter. We propose that the observations are related, and that the non-trivial scaling in the polymer system leads to time-dependent friction in a network, which in turn leads to a generalized Einstein relation operative in the intracellular environment. This results, in the driven system, in sub-ballistic motion at short times and sub-diffusive motion at longer times.

**9:30 AM T1.3**

**STRUCTURE OF CHARGED POLYMER CHAINS IN CONFINED GEOMETRY.** Jyotsana Lal, Elliot Gilbert, Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL; Loic Auvray, Laboratoire Leon Brillouin, Centre d'Etudes de Saclay, Gif-sur-Yvette Cedex, FRANCE.

Small-angle neutron scattering was used to study a model fully charged polyelectrolyte in bulk and when confined in porous Vycor glass. Appropriate mixtures of hydrogenated and deuterated poly(styrene sulphonate), which simultaneously satisfied the condition of zero average contrast and Vycor contrast matching, were used to measure intrachain correlations, for chain molecular weights between 25K to 450K Daltons. Fully deuterated solutions were also prepared enabling the separation of the intra- and interchain contributions to the total scattering. We have studied concentrations for which the chains are fully penetrated into Vycor. In the following paper we will discuss the measured intra- and interchain structures of the confined polyelectrolyte chains and compare and contrast these with those determined from scattering from the bulk.

**10:15 AM \*T1.4**

**BIOMOLECULES AND CELLS CONFINED IN SILICA NANOPORES.** J. Livage, Chimie de la Matière Condensée, Université Pierre et Marie Curie, Paris, FRANCE.

The sol-gel process opens new possibilities for biotechnology. Sol-gel glasses are formed at room temperature via the polymerization of molecular precursors such as metal alkoxides. Enzymes can be added to the solution of precursors. Hydrolysis and condensation lead to the formation of an oxide network in which bio-species remain trapped. Small substrate molecules can diffuse through the pores allowing reactions to be performed in-situ, inside the sol-gel glass. Trapped enzymes still retain their biocatalytic activity and may even be stabilized within the sol-gel cage.

Whole cell bacteria can also be immobilized within sol-gel glasses. They behave as a "bag of enzymes". Their membrane protects enzymes against denaturation and leaching. *Escherichia coli* induced for  $\beta$ -galactosidase were immobilized within sol-gel glasses. They are randomly dispersed within the silica matrix and that their cellular organization is preserved. The  $\beta$ -galactosidase activity of entrapped *E. coli* was studied using p-NPG as a substrate and the formation of p-nitrophenol was followed by optical absorption. These experiments show that *E. coli* still exhibit noticeable enzymatic activity after encapsulation, even on dried xerogels. Antibody-antigen recognition has been shown to be feasible within sol-gel matrices. Trapped antibodies bind specifically the corresponding haptens and can be used for the detection of traces of chemicals. Even whole cell protozoa have been encapsulated without any alteration of their cellular organization. For medical applications, trapped parasitic protozoa have been used as antigens for blood tests with human sera. Antigen-antibody interactions were followed by the so-called Enzyme Linked ImmunoSorbent Assays (ELISA).

**10:45 AM T1.5**

**COMPRESSIBILITY AND PARTIAL VOLUME CHANGES INDUCED BY HYDRATION AND PROTEIN FOLDING IN REVERSE MICELLES.** M. Waks, J.Y. Le Huérou, D. Valdez, Laboratoire d'Imagerie Paramétrique, CNRS, Paris, FRANCE; W. Urbach, Laboratoire de Physique Statistique de l'Ecole Normale Supérieure, CNRS, Paris, FRANCE.

The partial specific volume and adiabatic compressibility of macromolecules exquisitely reflect the hydration properties of their solvent-exposed surfaces, as well as their structure, dynamics and conformational states. Reverse micelles are protein-sized, optically clear, biomimetic microassemblies, where hydration can be experimentally controlled. The confining of proteins into such systems, induces conformational changes such as: partial unfolding or refolding to a more compact structure, depending on the initial state, the nature of the protein, or the surfactant used. We have explored by high-precision ultrasound velocimetry and densimetry four proteins:  $\beta$ -lactoglobulin, lysozyme, cytochrome c and myelin basic protein, confined in reverse micelles of an anionic surfactant, at different levels of hydration. We examine their partial specific volume and adiabatic compressibility and compare them to those obtained in aqueous solvents. For all proteins studied at the lowest water content, compressibility values are close to that of the theoretically estimated intrinsic compressibility. In addition, myelin basic protein, which displays in pure water, a high degree of conformational flexibility and disorder, refolds into a well-ordered, compact structure in reverse micelles. We have thus been able to follow by the above-mentioned techniques the transconformation of the same macromolecule from the aqueous unfolded to be a folded, micellar-confined conformation.

**11:00 AM T1.6**

**DYNAMICS OF SELF-SIMILAR SOL-GEL CLUSTERS AND BRANCHED MACROMOLECULES.** A.G. Zilman, R. Granek, Weizmann Inst. of Science, Dept. of Materials and Interfaces, Rehovot, ISRAEL.

The dynamics of flexible self-similar polymeric clusters, such as those appearing in sol-gel systems, is discussed. We use a linearized self-consistent approximation which is a generalization of the Doi-Edwards theory of linear polymers to objects of arbitrary fractal dimension. We calculate the mean-square displacement (MSD) of a monomer in a cluster and and viscoelastic modulus of a cluster. We find that when the hydrodynamic interaction is not screened (Zimm model) the MSD increases anomalously with time,  $MSD \sim t^\alpha$ , with a universal exponent  $\alpha \sim 2/d$  in  $d$ -dimensions, independent of the structural properties of a cluster, i.e. its fractal dimension  $d_f$  and the spectral dimension  $d_s$ . Such a behavior of MSD implies that the dynamic structure factor decays as  $\sim e^{-t^\alpha}$ . The viscoelastic modulus in the frequency domain behaves like  $G(\omega) \sim (i\omega)^u$  with  $u = d_f/d$ . When the hydrodynamics is screened (Rouse model, dense clusters), we find  $\alpha = 2/(2d_f)$  and  $u = d_f/(2d_f)$ . These results imply that the measurements of the dynamic structure factor and those of viscoelastic modulus are not independent. The comparison between the two can help to elucidate which type of dynamics is present. The results are supported by experimental results.

**11:15 AM \*T1.7**

**GLASS TRANSITION IN POLYMER GLOBULES.** Rose Du, MIT,

Dept of Physics, Cambridge, MA; Alexander Yu. Grosberg, Univ of Minnesota, Dept of Physics, Minneapolis, MN; Toyochi Tanaka, MIT, Dept of Physics, Cambridge, MA; Michael Rubinstein, Univ of North Carolina, Dept of Chemistry, Chapel Hill, NC.

We introduce a lattice model of glass transition in polymer globules. This model exhibits ergodicity breaking in which the disjoint regions of phase space do not arise uniformly, but as small chambers whose number increases exponentially with polymer density. Chamber sizes obey power law distribution, making phase space similar to fractal foam.

#### 11:45 AM T1.8

COMPUTATIONAL STUDY OF POLYMERIZATION IN CARBON NANOTUBES. Bradley M. Dickson, Steven J. Stuart, Clemson University, Dept of Chemistry; Bobby G. Sumpter, Donald W. Noid, Oak Ridge Natl Lab, Chemistry and Analytical Science Division, Oak Ridge, TN.

Carbon nanotubes may be filled with low-surface tension liquids and used as nanoscale reaction vessels. This has been performed by many researchers with a wide range of aqueous and metallic systems, but organic systems have not been widely studied. In this computational study, we examine polymerization in hydrocarbon fluids confined to the interior of carbon nanotubes. The simulations are performed via molecular dynamics with a newly developed model for hydrocarbons, the adaptive intermolecular reactive empirical bond-order potential (AIREBO) potential. This reactive potential allows for treatment of both intermolecular interactions and covalent bonding. It is found that thermally initiated polymerization of ethylene proceeds differently when confined to a nanotube than in the bulk liquid phase. Both the kinetics of the polymerization and the resulting polymer morphology are different when confined to nanoscale dimensions.

#### SESSION T2:

Chair: Rene M. Overney  
Monday Afternoon, November 27, 2000  
Room 313 (Hynes)

#### 1:30 PM \*T2.1

SYNCHROTRON X-RAY STUDIES OF MOLECULAR ORDERING IN CONFINED LIQUIDS. Oliver Seck, Hyunjung Kim, D.R. Lee, I.D. Kaendler, Deming Shu, Joydip Basu<sup>a</sup>, and Sunil K. Sinha, Advanced Photon Source, Argonne, IL. <sup>a</sup>University of Illinois, Urbana-Champaign, IL.

X-Ray specular and off-specular reflectivity studies have been carried out to study the density modulations in liquids confined between two smooth silicon mirrors. The special technical problems associated with this technique as well as the advantages of using high-energy and high-brilliance synchrotron x-ray beams for carrying out such experiments will be discussed. Results will be presented on the ordering of octamethylcyclotetrasiloxane (OMCTS) as a function of the confining pressure, where we find evidence of layering as the gap is decreased from macroscopic down to 1.99 nm.

#### 2:00 PM \*T2.2

DYNAMICS OF LAYERING TRANSITIONS OF CONFINED LIQUIDS. Miquel Salmeron and Friedrich Mugele<sup>a</sup>, Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, CA. <sup>a</sup>Current address: Universitaet Ulm, Abteilung Angewandte Physik, Ulm, GERMANY.

The layering transitions of octanol and undecanol confined between mica surfaces have been studied using a surface forces apparatus. Under confinement, the alcohols form bilayers of end-to-end H-bonded molecules. Upon compression, the bimolecules exhibit considerable deformation before expulsion. All but the two monolayers directly bound to the mica surface can be expelled. At any stage the confined bilayers exhibit liquid character with a viscosity almost equal to that of the bulk liquid. Only when the strongly bound monolayers come into contact at the highest load are solid effects in the form of stick-slip events manifested. The last layering transition of undecanol was studied by video microscopy. The study revealed that the transition starts with the nucleation of a 2-D void that expands within ~1 sec to cover the entire contact. The rapid expansion of the void leaves residual trapped pockets. The evolution of the 2-D void can be explained by the hydrodynamic model of Persson and Tosatti [Phys. Rev. B 50, 5590 (1994)].

#### 2:30 PM T2.3

VIBRATIONAL DYNAMICS OF CONFINED LIQUIDS. Alessandra Scodinu, Brian J. Loughnane and John T. Fourkas, Eugene F. Merkert Chemistry Center, Chestnut Hill, MA; Keisuke Tominaga, Department of Chemistry, Kobe University, JAPAN.

Time-resolved coherent spectroscopy has been used to study the intramolecular and intermolecular vibrational dynamics of liquids confined in nanoporous glasses. By studying the effects of polarization, temperature and pore size on the vibrational relaxation of confined liquids, we are able to develop a detailed microscopic picture of the structure and interactions between the liquid and the pore surfaces.

#### 3:15 PM \*T2.4

CHARGE AND GAS TRANSPORT IN POLYMER-ELECTROLYTE AND SOLID-OXIDE FUEL CELLS: INTERPLAY OF PHYSICS OF POROUS MEDIA AND ELECTROCHEMISTRY. Alexei A. Kornyshev, Research Center Juelich, Institute for Materials and Processes in Energy Systems, Research Center Juelich, Juelich, GERMANY.

The focus of this talk, an overview with original material, is on fundamental aspects of the theory of fuel cells related to the physics of charge and mass transport in confined systems. Its outline is as follows: 1. Introduction to fuel cells -objectives -components -problems -physics, chemistry & electrochemistry 2. Charge and gas transport in porous composite solid oxide fuel cell electrodes. Nonlinear transport theory versus percolation theory. Optimized structures for the best performance. 3. Proton transport in pores of polymer electrolyte membranes and polymer-electrolyte fuel cell electrodes. Charge transfer theory vs molecular dynamics. Improving proton transfer at lowering water and methanol mobility? 4. Summary: the finite size and confined volume effects; scaling aspects.

#### 3:45 PM T2.5

MODELING GAS SEPARATION MEMBRANES. Anthony P. Malanoski, The University of New Mexico, Dept of Chemical Engineering, Frank van Swol, Sandia National Laboratories and The University of New Mexico, Advanced Materials Laboratory, Albuquerque, NM.

Recent advances in the development and application of self-assembly templating techniques have opened up the possibility of tailoring membranes for specific separation problems. A new self-assembly processing route to generate inorganic membrane films has made it feasible to finely control both the three-dimensional (3D) porosity and the chemical nature of the adsorbing structures. Chemical sites can be added to a porous membrane either after the inorganic scaffolding has been put in place or, alternatively, chemical sites can be co-assembled in a one-step process. To provide guidance to the optimized use of these "designer" membranes we have developed a substantial modeling program that focuses on permeation through porous materials. The key issues that need to be modeled concern 1) the equilibrium adsorption behavior in a variety of 3D porous structures, ranging from straight pore channels to fractal structures, 2) the transport (i.e. diffusion) behavior in these structures. Enriching the problem is the presence of reactive groups that may be present on the surface. An important part of the design of actual membranes is to optimize these reactive sites with respect to their strength as characterized by the equilibrium constant, and the positioning of these sites on the adsorbing surface. What makes the technological problem challenging is that the industrial application requires both high flux and high selectivity. What makes the modeling challenging is the smallness of the length scale (molecular) that characterizes the surface reaction and the confinement in the pores. This precludes the use of traditional continuum engineering methods. However, we must also capture the 3D connectivity of the porous structure which is characterized by a larger than molecular length scale. We will discuss how we have used lattice models and both Monte Carlo and 3D density functional theory methods to tackle these modeling challenges.

#### 4:00 PM T2.6

PROBING CONFINED DYNAMICS OF WATER IN DISORDERED POROUS MEDIA BY NMR RELAXOMETRY AND NUMERICAL MODELING. Pierre Levitz, CRMD-CNRS, Orléans, FRANCE; Jean Pierre Korb, LPMC-CNRS, Ecole Polytechnique, Palaiseau, FRANCE; Alexandra Van-Quynh and Robert G Bryant, Chemistry Department, University of Virginia, Charlottesville, VA.

Disordered mesoporous materials with pore size ranging from 2 nm to some 10 nm develop large specific surface area. These matrices can be easily filled with polar fluids. In such a situation, the interfacial region between the solid matrix and the pore network strongly influence the molecular dynamics of the entrapped fluid. A promising way to probe such a coupling is to look at the NMR relaxation of the polar liquid using field cycling NMR relaxometry. We have performed such an experiment on a fully hydrated porous Vycor glass (1), free of electron paramagnetic impurities. The proton nuclear magnetic relaxation rate (1/T1) exhibits a logarithmic law on a large range of frequencies, mainly from 0.1 to 50 MHz. A cross-over is observed below 0.1 MHz. In order to understand the relationship between geometric disorder, interfacial confinement and magnetic relaxation, we first compute an

off-lattice reconstruction of the Vycor glass (2). Such a model does agree with available experimental data (specific surface, porosity, chord length distributions, small angle scattering and tortuosity). Based on recent neutron scattering studies of water dynamics inside Vycor glass, Brownian dynamics simulation is performed to analyze molecular self-diffusion and spin-lattice relaxation. Several conclusions can be stated: (i) The low frequency spin-lattice relaxation is dominated by intramolecular spin interactions (ii) Experimental field cycling NMR data are well reproduced and appear to be connected with the translational diffusion of water nearby the SiO<sub>2</sub> interface. (iii) The logarithmic character of the nuclear magnetic relaxation is related to the interfacial geometry of the Vycor glass. Several other multiconnected interfacial structures such as periodic minimal surfaces do not exhibit such an evolution. Extension of this work to different types of disordered porous media is in progress and will be presented. (1) P. Levitz, G. Ehret, S.K. Sinha, J.M. Drake. *J. Chem. Phys.* 6151-6161, Vol 95, (1991) (2) P. Levitz. *Advances in Colloid and Interface Science.* 76-77, pp 71-106 (1998)

#### 4:15 PM \*T2.7

FLOW, DIFFUSION, AND CONVECTION IN PERCOLATION CLUSTERS: NMR EXPERIMENTS AND COMPUTER SIMULATIONS. Rainer Kimmich, Andreas Klemm, Markus Weber, Univ of Ulm, Ulm, GERMANY.

Two- and three-dimensional percolation objects have been fabricated based on computer generated templates. Random site, semi-continuous swiss cheese, and semi-continuous inverse swiss cheese percolation models above the percolation threshold were considered. The model objects were filled with water and investigated using **NMR spin density and velocity mapping** after exerting a pressure gradient (A. Klemm et al., *Phys. Rev. E* 55 (1997) 4413). The spatial resolutions of the fabrication process and the micro-imaging experiments were 400 $\mu$ m and 200 $\mu$ m, respectively. The velocity resolution was 60 $\mu$ m/s. The fractal dimension, the correlation length, and the percolation probability were evaluated both from computer generated templates and corresponding NMR spin density maps. Based on velocity maps, the percolation backbones were determined. The fractal dimension of the backbones turned out to be smaller than that of the complete cluster. As further relations of interest, the volume averaged velocity as a function of the probe volume radius and the velocity correlation function of the percolating particles were evaluated. These dependences can partly be represented by hitherto unknown power laws. The results favorably compare to FEM simulations. In order to study the hindrance on diffusion by the matrix obstacles in static water, we have examined **interdiffusion** of water between compartments initially filled with H<sub>2</sub>O and D<sub>2</sub>O, respectively. The propagation of the diffusion front and the concentration profile can be described in accordance with the experimental fractal parameters as suggested by percolation theory and computer simulations. **Thermal convection** in a silicon oil filled site percolation object in Rayleigh/Bénard configuration was studied likewise using the same NMR methods. Simulations based on the finite volume method (FVM) were carried out for different porosities. Velocity maps indicate convection rolls spanning a few voxels up to the whole object. Histograms of the average velocity in the voxels reveal different limits that can be described by hitherto unknown power laws and identified with certain characteristics of the rolls.

#### 4:45 PM T2.8

POLYMER TRANSPORT ACROSS ISOTOPE SELECTIVE NANOMETRIC INTERDIFFUSION BARRIERS. Holger Gröll, Dept of Chemical Engineering, Ben-Gurion University, Beer-Sheva, ISRAEL; Alan R. Esker, Dept of Chemistry, Virginia Tech, Blacksburg, VA; Sushil K. Satija and Charles C. Han, NIST, Gaithersburg, MD.

Interdiffusion dynamics of compatible materials and the interfacial properties between incompatible materials have been extensively studied. In contrast, little experimental work has dealt with the properties of interdiffusion barriers inserted between two compatible polymer layers in order to alleviate direct contact. Here, we present an investigation of the diffusion dynamics of a polymer melt across a diffusion barrier formed by an interstitial nanometric membrane. Transport properties of the polymer melt across the membrane are strongly influenced by the membrane's thickness and compatibility with the adjacent polymeric material. In this case, isopentylcellulose cinnamate (IPCC) ultra-thin films (40 - 120 Å) were transferred on top of a spin-coated layer of a polymer (polymer A) using the Langmuir-Blodgett technique and subsequently photo cross-linked to create a permeable membrane. On top of the membrane, a polymer layer B was floated completing a trilayer "sandwich" type of sample geometry. Polystyrene of variable molecular weight served as polymer B and its deuterated analog as polymer A. In a series of annealing and quench experiments, the kinetics of polymer diffusion across the membrane was studied using neutron reflectivity measurements. For matched molecular weights of A and B, we observed faster transport

of the deuterated polymer across the barrier layer, leading to a volume change in the thin film system and a consequential displacement of the membrane. This observation indicates that the membrane is isotope selective. Varying the molecular weights and deuterium labeling of the polymers allows for a detailed characterization of the membrane's size discrimination and isotopic selectivity. The unique isotopic selectivity can be explained by subtle differences in the interactions between the different isotopically labeled polymers and the membrane material. Experiments with varying membrane thickness reveal a drastic change in polymer transport dynamics once the membrane thickness exceeds the polymer radius of gyration.

#### SESSION T3:

Chair: Pierre E. Levitz  
Tuesday Morning, November 28, 2000  
Room 313 (Hynes)

#### 8:30 AM \*T3.1

MOLECULAR DYNAMICS SIMULATIONS OF CONFINED GLASSFORMING FLUIDS. Fatollah Varnick, Peter Scheidler, Walter Kob, Kurt Binder, Institut fuer Physik, Johannes Gutenberg Universitaet Mainz, GERMANY, Jörg Baschnagel, Institut Charles Sadron, ULP, Strasbourg, FRANCE.

Two model studies are presented in order to elucidate the effect of confinement on glassforming fluids, attempting to eliminate the effect of attractive interactions between the confining walls and the fluid particles. In model I, short bead-spring chains (modelling a melt of flexible polymers) are put in between perfectly flat, structureless, walls on which repulsive potentials (decreasing with the 9th power of distance) act. It is shown that chains near the walls move faster (in the direction parallel to the walls) than chains in the bulk. A significant decrease of the (mode-coupling) critical temperature with decreasing film thickness is found. In model II, a binary Lennard-Jones liquid (80% A, 20% B particles) is confined in a narrow cylindrical pore, whose surface has an amorphous structure similar to the liquid. Although, as expected, the static structural properties of the liquid are not affected by the confinement, relaxation times near the wall are much larger than in the bulk. Consequences for the interpretation of experiments are briefly discussed.

#### 9:00 AM \*T3.2

RELAXATION MECHANISMS IN MUTUALLY SHEARING POLYMER BRUSHES. Jacob Klein, Rafael Tadmor, Joanna Janik<sup>a</sup>, Dept. Materials and Interfaces, Weizmann Institute, Rehovot, ISRAEL; Lewis Fetters, Exxon Research and Engineering, Clinton, NJ. <sup>a</sup>permanent address: Physics Dept., Jagellonian Univ., Cracow, POLAND.

Frictional drag between rubbing surfaces bearing end-tethered monolayers of polymers (brushes) with low glass-transition temperature, determined via high-resolution shear force measurements, attains a maximum on initial motion due to substantial elastic stretching of the chains. As the chains disentangle on further sliding, this falls by a cascade of relaxations to a value characteristic of kinetic friction, with a very weak velocity dependence. The weak shear velocity dependence results from the self-regulating nature of the mutual interpenetration zone within which the chain moieties are dragging. When sliding stops, the shear stress across the polymer layers decays by a process with a broad time spectrum, consistent with the relaxation of a network of dangling ends. These results shed light on the detailed molecular mechanism of frictional drag between compressed, mutually sliding brush layers.

#### 9:30 AM T3.3

DYNAMICS AND STRUCTURE OF FILLED POLYMERS AND INSIGHTS ON ULTRA-THIN POLYMER FILMS. Francis W. Starr, Thomas B. Schröder and Sharon C. Glotzer, Polymers Division and Center for Computational and Theoretical Materials Science, NIST, Gaithersburg, MD.

Significant enhancements in mechanical, rheological, dielectric, optical, and other properties of polymer materials can be obtained by adding fillers such as carbon black, talc, silica, and other inexpensive materials. The growing ability to design customized nano-fillers of arbitrary shape and functionality provides an enormous variety of property modifications by introducing specific heterogeneity at the nanoscale. However, detailed knowledge of the effects of fillers on a polymer melt at the molecular level is lacking due to the difficulty of directly probing the polymer structure and dynamics in the vicinity of the polymer-filler interface. In this regard, molecular simulations provide an ideal opportunity for direct insight into filled materials. To probe the effects of the filler on the local melt structure and dynamics, we perform molecular dynamics simulations of an idealized

polymer melt with chains having an end-to-end distance roughly equal to the facet size of a nanoscopic filler particle. Our findings show a strong similarity to those obtained for ultra-thin polymer films, suggesting that both ultra-thin films and filled-polymer systems might be understood in the same context. Specifically, we show that the glass transition temperature  $T_g$  of the melt, one of the most important processing parameters, can be shifted to either higher or lower temperatures by appropriately tuning the interactions between polymer and filler. A gradual change of the polymer dynamics approaching the filler surface causes the change in the glass transition. We also find that while the bulk structure of the polymers changes little, the polymers close to the surface tend to be elongated and flattened, independent of the type of interaction we study. Consequently, the dynamics appear strongly influenced by the interactions, while the melt structure is only altered by the geometric constraints imposed by the presence of the filler.

**10:15 AM \*T3.4**  
**MOLECULAR DYNAMICS OF THE INTERFACE BETWEEN WATER AND SELF-ASSEMBLED ORGANIC FILMS AS MODELS FOR LIQUID/LIQUID INTERFACES.** Ilan Benjamin, University of California, Department of Chemistry, Santa Cruz, CA.

We use molecular dynamics computer simulations to study the structure and dynamics of the interface between water and self-assembled organic monolayers which are designed to mimic several types of liquid/liquid interfaces. This results in a much better control over the structure of the interface. In particular, it is possible to study the interface intrinsic structure by removing the capillary broadening of the interface. Several types of organic surfaces, distinguished by their degree of roughness and by the nature of the organic terminating group, are considered.

**10:45 AM T3.5**  
**QUANTUM, CLASSICAL AND STATISTICAL MECHANICS OF MOLECULES IN NANOPORES: TUNNELING, PHASE TRANSITIONS AND ANOMALOUS DIFFUSION.** Scott M. Auerbach, Department of Chemistry, and Department of Chemical Engineering, University of Massachusetts, Amherst, MA.

Zeolites are nanoporous crystalline aluminosilicates with a rich variety of interesting properties and industrial applications. As important as zeolites are industrially, the physics underlying their application is poorly known. (i) We have developed a stable version of semiclassical harmonic transition state theory, which when applied to calculating proton transfer rates in zeolites shows that tunneling dominates up to and slightly above room temperature, and that true proton transfer barriers are being underestimated by some experiments. (ii) We have applied grand canonical lattice simulation techniques to demonstrate that cooperative interactions can lead to phase transitions for benzene in Na-X at high temperatures, and have explored the consequences of this type of phase transition for diffusion in zeolites. (iii) For single-file host-guest systems, phase transitions cannot occur, but repulsive guest-guest interactions can lead to anomalous diffusion, which has been observed experimentally. We have developed a theory for self diffusion in single-file Langmuirian zeolites of finite extent, which shows that Fickian diffusion re-emerges in single-file systems well before desorption from the zeolite, suggesting that Fickian self diffusion dominates transport in longer single-file zeolites.

**11:00 AM T3.6**  
**MOLECULAR DIFFUSION AND CONFINED GEOMETRIES: REVISITING ANALYSIS OF NMR-PGSE EXPERIMENTS.** Stephane Rodts, Laboratoire Central des Ponts et Chaussées, Ministère de l'Équipement, Champs-sur-Marne, FRANCE; Pierre Levitz, Centre de Recherches sur la Matière Divisée, CNRS, Orleans, FRANCE.

We report both theoretical and experimental developments aiming at interpreting Pulsed Gradient Spin Echo (PGSE) (1) data for self-diffusing fluids in saturated macroporous media. Our approach consists in analysing the time dependence of the PGSE amplitudes for each single gradient strength. It differs from the well documented method which relies on an analysis of the PGSE amplitude gradient dependence at fixed diffusion times (2,3). In our analysis, two pieces of information are extracted from different time scales: -'short time scale': we define a diffusion coefficient as being dependent on the length scales in the material. -'long time scales': the PGSE amplitude is sensitive to the dimensionality of the material. This behaviour is related to the long time evolution of the self diffusion propagator. Length scale dependent diffusion coefficient were measured in water-saturated random close packing (RCP) of monodisperse glass beads. These coefficients were found to give an insight in the micro-macro transition for diffusive transport. The main feature of this transition is a global decrease of water diffusion coefficient from the bulk value to the macroscopic one. We give numerical evidence that this global decrease is not monotonic, and that the diffusion

coefficients go through a minimum, characteristic of a slowing down exploration of the pore network at some defined length scale. The long time behaviour of echo amplitudes was investigated both in RCP and in a system of parallel plastic platelets with rough surface. Echo amplitudes were found to obey a decaying algebraic law with time, with exponents  $-d/2$ , where  $d$  is the dimensionality of the system. 1. Stejskal E.O. & al., J. Chem. Phys., (1965), **42**, 288 2. Mitra P.P., Physica A, (1997), **241**, 122 3. Schwartz L.M. & al., Phys. Rev. E, (1997), **55**, 4225

**11:15 AM \*T3.7**  
**A PERCOLATION APPROACH OF PROTON NUCLEAR SPIN-LATTICE RELAXATION IN ROTATIONALLY IMMOBILIZED PROTEINS AND OTHER IMPERFECTLY PACKED SOLIDS.** Jean-Pierre Korb, Laboratoire de Physique de la Matière Condensée, CNRS UMR 7643, Ecole Polytechnique, Palaiseau, FRANCE; Alexandra Van Quynh, Robert G. Bryant, Chemistry Department, University of Virginia, Charlottesville, VA.

The magnetic field dependence of proton spin-lattice relaxation rates in semi-solids such as engineering polymers, protein gels, solid proteins, noncrystalline solids, and biological tissues is described by a power law,  $1/T_1 = Af^{-b}$ , where  $f$  is the Larmor frequency,  $A$  and  $b$  are constants. The value of  $b$  is often 0.5 or near 0.5 which suggests that the spin-lattice relaxation is dominated either by a spin-diffusion process or by a quasi mono-dimensional molecular dynamics. However, the  $b$  values different from 0.5 are now common. For example, in polymers like polycarbonate,  $b$  is about 0.6. In a dry rotationally immobilized protein,  $b$  is found between 0.65 and 0.85. When water is added to the protein,  $b$  is found between 0.50 and 0.62 depending on the level of hydration. These systems are nonuniformly packed. The distribution of intra and inter molecular contacts forms an imperfect mechanical network that may affect spin relaxation. The magnetic dipolar coupling between the proton spins also creates an incompletely connected network. Here, we show that the concepts of the percolation theory lead to a quantitative description of the field dependence of nuclear spin-lattice relaxation of the solid protein protons. The magnetic field dependence of the relaxation rate,  $1/T_1$ , directly reflects low frequency protein structural fluctuations, which propagate like a vibration along the backbone carbon chains and modulate the dipole-dipole interaction of the non mobile neighboring proton spins. These effects on the spin-lattice relaxation in proton systems have very important implications for magnetic imaging as well as for characterization of engineering polymers.

**11:45 AM T3.8**  
**REACTION KINETICS EFFECTS ON REACTIVE WETTING.** Marta Gonzalez, Departamento de Física, Universidad Central de Venezuela; Mariela Araujo, Reservoir Department, PDVSA Intevep, Caracas, VENEZUELA.

Chemical reactions at the interface between two liquids and a solid can lead to complex situations. For example, after the reaction the substrate may become less wettable allowing the formation of running droplets. We propose a model where droplets of fluids of a given radius, are injected into a porous system represented by a Hele-Shaw cell. In their advance, the droplets react chemically with the solid surface, making it less wettable. The velocity of the droplet after the reaction is calculated for different reaction kinetics including adsorption, for situations where gravity effects are negligible. In all cases, a transition from a Brownian motion regime to a ballistic displacement is observed. This transition is associated to scaling effects. The model is able to describe the situation of partial wetting, where a droplet lying on a horizontal surface, tends to escape from a region after the reaction, moving with a constant velocity. In the hydrodynamic regime, the motion of the reactive droplets depends on the order of the reaction.

SESSION T4:  
 Chair: J. M. Drake  
 Tuesday Afternoon, November 28, 2000  
 Room 313 (Hynes)

**1:30 PM \*T4.1**  
**SCALING EFFECTS OF SHEARING JUNCTIONS.** Jacob Israelachvili, Delphine Gourdon, College of Engineering; Jean Carlson, Physics; University of California (UCSB), Santa Barbara, CA.

Shear measurements made with the Surface Forces Apparatus have revealed surprisingly long relaxation times and large characteristic memory distances during lubricated sliding, i.e., sliding with a thin fluid layer confined between two molecularly smooth surfaces. The main differences between lubricated and unlubricated or 'dry' sliding

will be compared, especially in regard to the relaxation processes occurring at the molecular and microscopic levels. We are also studying the question of whether there exists a universal 'scaling' for junctions having different dimensions (e.g., contact areas), pressures and elastic constants, which is important for understanding tribologically-associated mechanisms such as the friction of rough or heterogeneous surfaces (in contrast to ideal, molecularly smooth surfaces undergoing wearless sliding), material failure such as fracture and wear, and geological movement such earthquakes, avalanches and landslides. The ability to model the observed behavior using simple rate-and-state models, and the physical meaning of the fitted parameters, will be discussed.

#### **2:00 PM \*T4.2**

**FRICION AT THE CONTINUUM LIMIT – WHERE IS THE BOUNDARY?** Steve Granick, University of Illinois, Dept. of Materials Science, Urbana, IL.

Films whose thickness exceeds a few molecules but is less than macroscopic have been insufficiently considered. Here, we show that the classical no-slip boundary condition, believed to describe macroscopic flow of low-viscosity fluids, overestimates hydrodynamic forces starting at lengths corresponding to hundreds or thousands of molecular dimensions when water or tetradecane is placed between smooth nonwetting surfaces whose spacing varies dynamically. When hydrodynamic pressures exceed 0.1-1 atmospheres (this occurs at spacings that depend on the rate of spacing change), flow becomes easier than expected. Therefore solid-liquid surface interactions influence not just molecularly-thin confined liquids but also flow at larger length scales. This points the way to strategies for energy-saving during fluid transport and may be relevant to filtration, colloidal dynamics, and microfluidic devices.

#### **2:30 PM T4.3**

**MACROSCOPIC VERSUS MICROSCOPIC DESCRIPTION OF FRICTION: FROM TOMLINSON MODEL TO SHEARONS.** Veaceslav Zolj, Cornell Univ, Dept of Computer Science, Ithaca, NY; Markus Porto, Michael Urbakh, Joseph Klafter, Tel Aviv Univ, School of Chemistry, ISRAEL.

We investigate the response of an embedded system subject to an external drive, which is chosen to be either a constant velocity or a harmonic shear. Two approaches are introduced which cover macroscopic and microscopic aspects of the problem and mimic recent measurements on friction using surface force apparatus. We propose a method for analyzing both linear and nonlinear response of confined systems driven harmonically. The method provides a way to deduce the microscopic parameters responsible for dissipation. The shear is shown to excite "shearons", which are collective modes of the embedded system with well-defined spatial and temporal patterns that dominate the frictional properties of the driven system. We demonstrate that the slip relaxation in stick-slip motion and memory effects are well described in terms of the creation and or annihilation of shearons.

#### **3:15 PM \*T4.4**

**THE INTERFACIAL DYNAMICS OF CONTACTS PROBED USING DIFFERENT NANOSCALE EXPERIMENTAL TOOLS.** Virginie Pasquier and J.M. Drake, Exxon Mobil Research and Eng. Co., Annandale, NJ.

The dynamics of interfacial forces, in response to an applied stress, are intimately related to the deformability of the material in the contact. We report on those processes that occur during the formation and breaking of nanoscale and microscale contacts. Using bare silica as interface material with or without adlayers, we study these systems using experimental nano-tools consisting of Nanoindenter, Atomic Force Microscope and Surface Force Apparatus. Elastic and viscoelastic mechanical response of these contacts to both normal and shear stresses will be discussed.

#### **3:45 PM T4.5**

**USING SMALL VIBRATIONS TO CONTROL FRICTION AT THE NANOSCALE.** Y. Braiman and V. Protopenescu, Center for Engineering Science Advanced Research, Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Recently, several groups demonstrated that friction [1,2] and chaos in friction [3] can be controlled and significantly reduced either by applying very small, intently focused control perturbations to the sliding system or by introducing quenched disorder onto the substrate [4]. These results point to completely new directions for realizing robust ultra-low friction in nano-mechanical devices, which steer away from the traditional lubrication techniques. We studied the response of a nano-array of atoms to the mechanical vibration of their substrate, within the minimalist model of friction. Our motivation is

twofold, namely: (i) understanding the basic mechanisms of frictional response to small periodic and random perturbations and (ii) developing robust control techniques for friction. Numerical simulations of the model suggest that the friction coefficient undergoes a sharp transition to the regime of very small values when the amplitude of the vibration reaches a critical threshold. We find a strong correlation between the friction coefficient and the phase synchronization of the sliding array. In particular, at the transition point, we observe a significant increase in the phase synchronization of the array. We estimate analytically the transition point and contrast the effects of periodic and random surface vibrations on the friction coefficient. This work is sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-00OR22725 with UT-Battelle, LLC. 1. M. Heuberger, C. Drummond, and J. Israelachvili, *J. Phys. Chem. B* **102**, 5038 (1998). 2. J. Gao, W.D. Luedtke, and U. Landman, *J. Phys. Chem. B* **102**, 5033 (1998). 3. M.G. Rozman, M. Urbakh, and J. Klafter, *Phys. Rev. E* **57**, 7340 (1998). 4. Y. Braiman, F. Family, H.G.E. Hentschel, C. Mak, and J. Krim, *Phys. Rev. E* **59**, R4737 (1999). "This submitted manuscript has been authored by a contractor of the U.S. government under Contract No. DE - AC05 - 00OR22725 with UT - Battelle, LLC. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

#### **4:00 PM T4.6**

**FRICION, WEAR, AND THIRD-BODY PROCESSES STUDIED BY REAL-TIME RAMAN TRIBOMETRY.** S.D. Dvorak, K.J. Wahl, and I.L. Singer.

The study of coatings tribology is challenging because the coating material often changes during sliding, and the materials present at the sliding interface are often very different from the original material pair, or 'third bodies'. The thin interfacial films and debris, or 'third bodies', which form under pressure during sliding undergo a variety of changes (e.g. thinning, agglomeration, retransferring, oxidation) inside the contact where real-time detection and analysis are very difficult. We study the friction between a transparent hemispherical slider and a coated substrate with a Raman tribometer capable of examining the buried interface during sliding. Real-time video micrographs and Raman spectra monitor third body formation, dynamic behavior, and degradation over the life of the sliding contact. Simultaneous friction measurement allows the correlation of changes in the third body to changes in friction. Experiments on MoS<sub>2</sub> and Pb-Mo-S coatings revealed evolution of interfacial chemistry and third body processes (detachment, transfer, and ejection of debris). Varying the environment between dry and humid air resulted in changes in friction from ~0.03 to 0.2; visualization and Raman analyses of the contact revealed variation in the sliding accommodation mode but little change in transfer film chemistry. The dynamic response of the third body to abrupt changes in humidity will also be discussed.

#### **4:15 PM \*T4.7**

**PHYSICS OF ATOMIC-SCALE STICK SLIP.** E. Meyer, R. Bennewitz, M. Bammerlin, M. Guggisberg, T. Gyalog and E. Gnecco, Institute of Physics, University of Basel, Basel, SWITZERLAND.

Atomic-scale stick-slip is one of the fundamental friction processes. It has been observed on layered materials, such as graphite, or ionic crystals, such as NaCl(001). Recently, wearless friction was also observed on clean metallic surfaces, such as Cu(111). The friction force vs. lateral position traces show stick slip with the periodicity of the atomic lattice. The probing tip sticks at certain positions, builds up elastic deformation until an instability occurs. Then, the tip jumps one unit cell to the next sticking site. Friction force loops show that the energy which is released during one slip is typically 1eV. The velocity dependence of atomic-scale stick-slip was investigated. A logarithmic dependence of friction as a function of velocity is found. The results are discussed in terms of an extended Tomlinson model, which takes into account thermal activation. At low velocities, the tip may slip at lower lateral forces because of thermal activation. At higher velocities the probability is lower to overcome the barrier by thermal activation. Experiments with oscillating cantilevers show that dissipation is also observable in the purely attractive force regime. Possible mechanisms, such as instabilities in the vertical direction, will be discussed.

#### **4:45 PM T4.8**

**INFLUENCE OF BOUNDARY CONDITIONS ON THE TRIBOLOGICAL BEHAVIOR OF THIN FILMS CONFINED BETWEEN TWO WALLS.** Martin Müser, Johannes Gutenberg-Universität, Inst. für Physik, Mainz, GERMANY.

The tribological behavior of thin confined films is investigated by means of molecular dynamics simulations. It is shown that the way in which shear is imposed strongly influences the frictional forces between the film and the confining walls. In particular, we contrast

simulations done at constant lateral velocity of the top wall to simulations where the top wall is pulled via a weak elastic spring (stick-slip regime). We also compare constant normal force to constant separation simulations. The results are interpreted in terms of the Tomlinson model and a recently suggested theory for the interaction between two walls separated by a sub monolayer of physisorbed atoms.

#### SESSION T5:

Chair: Michael Urbakh  
Wednesday Morning, November 29, 2000  
Room 313 (Hynes)

#### 8:30 AM \*T5.1

SLIDING TRANSITIONS, MECHANICS AND DISSIPATION IN NANOSCALE CONTACTS. K.J. Wahl, U.S. Naval Research Laboratory, Washington, DC; S.A. Syed Asif, Dept. of Materials Science and Engineering, Univ. of Florida, Gainesville, FL; R.J. Colton, U.S. Naval Research Laboratory, Washington, DC.

In order to investigate tribological processes and adhesion at the nanometer scale, we need to better understand how model asperity contacts respond to shear and dissipate energy. In our experiments, we investigate the dynamic processes occurring during the transition from static to sliding contact, as well as during the formation and breaking of nanoscale adhesive contacts. We have implemented approaches combining AC modulation techniques with both AFM and hybrid nanoindentation (depth-sensing nanoindentation with AFM imaging capabilities). Both amplitude and phase response of the contacts are monitored using lock-in amplifiers, and dynamic models are used to interpret the response of the contacts to shear and normal forces. For sliding contacts, we incorporate harmonic analysis of the response of the contact to lateral modulation; as a result, we are now able to distinguish between various types of dissipation including friction, microslip and damping. We demonstrate application of this technique to discriminate between static to sliding contacts as well as identify and quantify microslip in nanoscale contacts. Alternatively, for contacts that are not sliding, the modulation approach allows determination of the localized mechanical properties of monolayers and polymer thin films and surfaces (e.g. loss and storage moduli, hardness, damping losses) as well as examination dynamic processes that occur during the formation and breaking of nanoscale contacts.

#### 9:00 AM \*T5.2

BOUNDARY LUBRICATION: LAYERING TRANSITION FOR CURVED SOLID SURFACES WITH LONG-RANGE ELASTICITY. B.N.J. Persson, IFF, FZ-Juelich, GERMANY.

The properties of an atomic lubricant confined between two approaching surfaces are investigated by molecular dynamics. In the limit of thin interfaces, the lubricant atoms form well defined layers, whose number decreases in discontinuous steps with increasing applied pressure. These transitions occur easily and completely for unpinned lubrication films, while they are sluggish and incomplete in the case of strong pinning. Before the transition, an intermediate phase arises, which facilitates the thinning of the lubricant. Lateral sliding of the surfaces enhances the thinning rate. I also show that for two-dimensional liquid-like layers, the squeeze-out exhibit instabilities which may result in trapped islands of lubrication molecules, as observed in recent experiments.

#### 9:30 AM T5.3

THERMODYNAMICAL AND MECHANICAL PROPERTIES OF HOLLOW NANOPARTICLES. Ulrich S. Schwarz, Samuel A. Safran, Shigeyuki Komura, Weizmann Institute, Dept of Materials and Interfaces, Rehovot, ISRAEL.

When layered crystals such as C, WS<sub>2</sub>, BN and GaAs are restricted to finite sizes, they generally form single- and multi-walled hollow nanoparticles in order to avoid dangling bonds. This can happen either in gas-phase synthesis or after violent disruption of the layered structure. Another class of hollow nanoparticles are colloidal core-shell particles which in principle offer better control of size and shape. Using continuum approaches to model van der Waals interaction and elastic deformation, we investigate theoretically some unusual properties of spherical hollow nanoparticles. Since the attractive interaction between two such nanoparticles scales linearly with their radius R, the heat of sublimation of the solid becomes much larger than for molecular scale van der Waals solids. Our model also shows that the interaction range scales inversely with R. This results in the disappearance of the gas-liquid coexistence from the phase diagram for particle radii in the range of 1-3 nm (depending on wall thickness). We also show that the mechanical stability is limited by forces in the nN range and pressures in the GPa range, as evidenced by recent friction experiments with multi-walled WS<sub>2</sub> nanoparticles.

#### 10:15 AM \*T5.4

IMAGING AND SPECTROSCOPY AT THE SINGLE MOLECULE LEVEL WITH CARBON NANOTUBE PROBES. Charles M. Lieber, Harvard University, Department of Chemistry, Cambridge, MA.

Scanning probe microscopies, such as atomic force microscopy, represent important tools for investigating phenomena at the nanometer scale, although the resolution and sensitivity are limited by the nature of the probe tip. Carbon nanotubes are materials that can overcome the limitations of conventional probe tips and thus offer great potential for the future. In this presentation the fabrication, properties and applications of carbon nanotube probes will be reviewed. First, chemical vapor deposition approaches will be described which allows simple and reproducible fabrication of individual single-walled nanotube tips with radii less than 2 nm. The mechanical properties and resolution of these tips will be discussed. Second, application of single-walled nanotube tips for high resolution imaging of complex soft matter, such as large proteins and protein nucleic acid complex will be presented. Third, highly selective strategies for the modification of nanotube probe ends have been developed and used to probe intermolecular forces in a detailed manner. The use of modified nanotube tips for mapping spatial variations in chemical functionality down to the molecular scale will be described. Future directions and challenges with nanotube probe tips will be discussed.

#### 10:45 AM T5.5

IMAGING THREE-DIMENSIONAL SINGLE MOLECULE ORIENTATIONS IN CONFINED ENVIRONS. Andrew P. Bartko, Robert M. Dickson, School of Chemistry and Biochemistry, Atlanta, GA.

Providing previously obscured positional and orientational information, novel wide-field optical microscopy methods capable of visualizing 3-D orientational dynamics of individual room temperature molecules have been developed. Utilizing a single detector, this facile method enables simultaneous observation of all molecular orientations without polarization optics. Such methods not only provide conclusive, nondestructive evidence of single molecule observation, but also make single molecule orientational studies accessible to a wide range of researchers. Analysis of observed molecular emission patterns not only directly and noninvasively reveals true three-dimensional orientational dynamics of individual molecules, but also directly probes spatial heterogeneity in polymeric systems far below the glass transition temperature.

#### 11:00 AM T5.6

VELOCITY DISTRIBUTION OF ELECTRONS ESCAPING FROM A POTENTIAL WELL. James P. Lavine, Eastman Kodak Company, Rochester, NY.

Particles confined by geometry [1] or by potential wells [2,3] have the opportunity to escape over time, and the time scale for this process is found by a variety of computational methods [1-3]. The present work considers the velocity distribution of electrons escaping from a confining potential well. The goal is to relate the velocity distribution and the time scale for escape to the details of the interactions between the electrons and the phonons. The initial rounds of calculations base the time between electron-phonon scatterings on the electron's mobility and move the electron in a constant field according to Newton's equation of motion between scattering events. In addition, the electron's energy is reset to the phonon energy after a scattering. The simplest model uses a fixed phonon energy and the escaping electron velocity distribution is strongly peaked. The next models allow a range of phonon energies, and the escaping electron velocity distribution is broad after a sharp threshold. As expected, the characteristic time for escape depends upon the phonon energy model. The spatial distributions of the electrons at selected times are also captured and these are peaked at the potential minimum. This set of results is contrasted with those from the use of more realistic and more detailed models of electron-phonon scattering. The escaping electron velocity distribution is also compared with that from the traditional model of thermionic emission. 1. R. Metzler and J. Klafter, MRS Symp. Proc. 543, 281 (1999). 2. H.A. Kramers, Physica 7, 284 (1940). 3. J.P. Lavine, E.K. Banghart, and J.M. Pimbley, MRS Symp. Proc. 290, 249 (1993).

#### 11:15 AM \*T5.7

COLLECTIVE ELECTRONIC-EXCITATIONS IN CONJUGATED DENDRIMERS AND PHOTOSYNTHETIC ANTENNAE. Shaul Mukamel, Vladimir Chernyak, University of Rochester, Department of Chemistry, Rochester, NY; Sergei Tretiak, Los Alamos National Laboratory, Theoretical Division, Los Alamos, NM.

A microscopic procedure for dissecting aggregates into effective independent chromophores is presented and applied to the chlorophylls and carotenoids in photosynthetic antennae and to

Phenylacetylene Dendrimers. The distribution of cooperative radiative decay rates is calculated. This distribution which depends on both the exciton coherence sizes and aggregate geometry can be directly observed using single-molecule spectroscopy. Electronic excitations of the LH2 antenna complex and of Phenylacetylene Dendrimers are analyzed using collective electronic normal modes representing the changes in charge and bond-order distributions induced by the optical field. Two-dimensional plots of these modes show that in dendrimers the relative motion of electron-hole pairs is sharply confined by *meta*-conjugation. Self-similarity and the high degree of symmetry utilized by decomposing the space of optical excitations into irreducible representations make it possible to compute the one-exciton states and the linear and nonlinear optical response with reduced numerical effort that scales linearly rather than exponentially with the number of generations. The optical response is dominated by localized excitons belonging to the periphery. Absorption spectra of Phenylacetylene Dendrimers are analyzed using these modes. A direct relationship is established between the superradiance enhancement factor  $L_S$  and the exciton coherence size  $L_p$  associated with the off-diagonal density matrix elements in the molecular representation. Various factors which affect the latter, including finite temperature, energetic disorder, coupling with phonons, and polaron formation are explored. Applications are made to photon-echo and pump-probe spectroscopies of the B850 system of the LH2 antenna in purple bacteria. A microscopic description of nonlinear optical spectroscopies of confined excitons starting with the Frenkel-Heitler-London Hamiltonian is presented using the nonlinear exciton equations (NEE). The equations follow explicitly the complete set of dynamical (one-, two-, and three-point) exciton variables relevant for the third-order response. Effects of nuclear motions are incorporated through relaxation superoperators calculated perturbatively in exciton-phonon coupling. A closed expression for the third order response is derived by solving the (NEE). These results set the stage for designing multidimensional spectroscopies of excitons and analyzing them using coherence-transfer pathways. "Scaling Of Fluorescence Stokes Shift And Superradiance Coherence Size In Disordered Molecular Aggregates," V. Chernyak, T. Meier, E.V. Tsiper, and S. Mukamel, *J. Phys. Chem.*, **103**, 10294-10299 (1999). "Frenkel-exciton Hamiltonian for Dendrimeric Nanostar," T. Minami, S. Tretiak, V. Chernyak, and S. Mukamel, *J. Lum.*, **87-89**, 115-118 (1999). "Exciton-Hamiltonian and Delocalized Electronic Excitations in the LH2 Antenna Complex of Purple Bacteria," S. Tretiak, C. Middleton, V. Chernyak, and S. Mukamel, *J. Phys. Chem. B.*, **104**, 4519-4528 (2000). "Two-Exciton States and Spectroscopy of Phenylacetylene Dendrimers", V. Chernyak, E. Y. Poliakov, S. Tretiak and S. Mukamel, *J. Chem. Phys.*, **111**, 4158-4168 (1999).

#### 11:45 AM T5.8

STATIC FRICTION BETWEEN ELASTIC SOLIDS DUE TO RANDOM ASPERITIES. J.B. Sokoloff, Physics Department and Center for Interdisciplinary Research on Complex Systems, Northeastern University, Boston, MA.

Several workers have established that the Larkin domains for two three dimensional nonmetallic elastic solids in contact with each other at a disordered interface (i.e., domains over which the solids are able to distort to accommodate the disorder at the interface) are enormously large. On the basis of this fact one is forced to conclude that there should be negligible static friction per unit area of contact between two elastic solids. In order to account for the virtually universal occurrence of static friction when two bodies are in contact, several workers have proposed that in order to have it, there must exist a submonolayer film of "lubricant" molecules at the interface between the two solids. The present work argues that the fluctuations in the heights of the random asperities at the interface that occur in the Greenwood-Williamson model can account for static friction, even in the absence of such lubricant films.

#### SESSION T6:

Chair: Shaul Mukamel  
Wednesday Afternoon, November 29, 2000  
Room 313 (Hynes)

#### 1:30 PM \*T6.1

SINGLE-MOLECULE DYNAMICS. Xiaoliang Sunney Xie, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA.

Information regarding molecular interactions and chemical dynamics has come almost exclusively from experiments conducted on large ensembles of molecules. Although ensemble-averaged results are essential, they often preclude detailed information because of the lack of a priori knowledge of the distributions and fluctuations of molecular properties. Recent advances in single-molecule spectroscopy allow direct measurements of the distribution of a molecular property and its dynamical fluctuation, revealing information hidden in the

ensemble averaged experiments. The single-molecule methodology has changed the way problems are approached. New insights using this methodology are beginning to emerge. The techniques are still evolving; new imaging tools are being developed, especially for imaging single biomolecules and visualizing their chemical reactions in living cells.

#### 2:00 PM \*T6.2

OBSERVATION OF LASER SPECKLE EFFECTS IN AN ELEMENTARY CHEMICAL REACTION. Eric Monson, Raoul Kopelman, University of Michigan, Department of Chemistry, Physics and Applied Physics, Ann Arbor, MI.

An experimental demonstration is provided for memory-based, nonclassical reaction kinetics in a homogeneous system with an elementary reaction,  $A \rightarrow C$ . A new reaction-kinetics regime is observed which is a direct consequence of speckles in the laser beam. However, in spite of the nonrandom, speckled initial distribution of reactant B, the long-time regime gives the first experimental demonstration of the asymptotic self-segregation ('Zeldovich') effect. Monte Carlo simulation results are consistent with the experiments.

#### 2:30 PM T6.3

LEVY DISTRIBUTION OF SINGLE MOLECULE LINE SHAPE CUMULANTS IN GLASSES. E. Barkai, R. Silbey and G. Zumofen, Dept of Chemistry, Massachusetts Institute of Technology, Cambridge, MA.

Experimental advances have made it possible to measure the spectral line shape of a single molecule (SM) embedded in a condensed phase. Because each molecule is in a unique static and dynamic environment, the line shapes of chemically identical SMs vary from molecule to molecule. In this way, the dynamic and static properties of the host are encoded in the distribution of single molecule spectral line shapes. We examine the statistical properties of the line shapes and show how these are related to the underlying microscopic dynamical events occurring in the condensed phase. We use the Kubo-Anderson approach to model the line shape of a single molecule in a low temperature glass described by the standard tunneling model (Anderson, Halperin, Varma and Philips). In this model, a random distribution of low-density dynamical defects [e.g., spins or two level systems (TLS)] interacts with the molecule via *long range interaction* (e.g., dipolar). We show that Lévy statistics fully characterize the properties of the SM spectral line both in the *fast* and *slow modulation limits*. The spectral line is characterized by its cumulants,  $\kappa_j$  ( $j = 1, 2, \dots$ ) that vary from molecule to molecule. We show that the probability densities  $P(\kappa_1)$  and  $P(\kappa_2)$  are symmetrical and one sided Lévy stable laws, respectively, while higher order cumulants are described by Lévy statistics only in the *slow modulation limit*. We then compare our analytical results, derived in the slow modulation limit, with results obtained from numerical simulation based on the standard tunneling model of glass. The good agreement indicates that the slow modulation limit is correct for the parameter set relevant to experiment, thus generalized central limit theorem is applicable for this problem. We then show that Lévy statistics can be used to analyze other statistical properties of SMs in disordered media, including the theory of inhomogeneous line broadening.

1. E. Barkai, R. Silbey and G. Zumofen *Phys. Rev. Lett.* **84** 5339 (2000).
2. E. Barkai and R. Silbey, *Chem. Phys. Lett.*, **310** 287 (1999)

#### 3:15 PM \*T6.4

MECHANICAL AND TRIBOLOGICAL MEASUREMENTS AT A SUBMICROMETRIC SCALE. Christian Fretigny, ESPCI/LPQ, CNRS ESA 7069, Paris, FRANCE.

Characterizations of small size contacts are now currently realized using force microscopy. A brief review of the available methods is given. Though qualitative information can easily be get from this technique, quantitative data is generally more difficult to extract. The example of contact on polymers which are viscoelastic at the experimental temperature is presented. Adhesion kinetics and transition towards sliding friction of the tip are described. Since contact radius can be determined in this case, the viscoelastic modulus of the polymer is deduced from stiffness measurements. Spatial resolution of this determination is about one micrometer. For less compliant materials or very thin films, resolution is expected to be higher. However, since the contact radius is then not easily estimated, only loss angle can be determined. Finally, the occurrence of a stick-slip regime is discussed. Though the static contact is well analyzed from stiffness measurements, sliding contact is more difficult to study. Such a description should be valuable, for fundamental purposes as well as for mechanical imaging. Contact radius being reduced compared to the static case, resolution of the characterization is expected to be high. A method is presented which uses the excitation of the cantilever resonance when the tip is in contact with the surface. Its applicability for mechanical and tribological



measurements is discussed. Experimental results on silanized surfaces and heterogeneous materials will be presented.

#### 3:45 PM **T6.5**

ADSORPTION IN ORDERED POROUS SILICON: A RECONSIDERATION OF THE ORIGIN OF THE HYSTERESIS IN THE LIGHT OF NEW EXPERIMENTAL OBSERVATIONS. B. Coasne, A. Grosman, C. Ortega, M. Simon Groupe de Physique des Solides, UMR 7588, Universités Paris 7 & 6, FRANCE.

Porous silicon formed in highly boron doped [100] single crystal silicon exhibits some microstructural properties which are of great interest for a better understanding of the fluid behaviour in confined media. This ordered mesoporous material which is obtained by electrochemical etching in a HF solution exhibits an anisotropic morphology with pores perpendicular to the substrate and separated from each other by silicon walls  $\sim 10$  nm thick. The pore sections of polygonal shape have sizes between 50 and 250 Å. The top of these non interconnected pores are in contact with the gas so that pore blocking effect could not occur. Moreover, the porous silicon part can be separated from the substrate to obtain a porous silicon membrane. It is thus possible to study, for the first time, the sorption isotherm on a same porous material with pores opened at one or at both ends in order to check an old but always current idea based on the Kelvin description of the capillary condensation which suggests that the sorption should occur reversibly in the first case and irreversibly in the second one.

Adsorption of krypton and nitrogen at 77K have been performed with a volumetric technique. The type IV isotherms obtained exhibit a large hysteresis loop whether the pores are opened at one or both ends. The adsorption branches are representative of the pore size distribution according to the Kelvin equation while the position and the abruptness of the desorption branches can not be explained by this model. These results indicate that the system goes through metastable states during the desorption process. To our knowledge the models providing the existence of such states do not explain these results.

#### 4:00 PM **T6.6**

ADSORPTION AND PHASE SEPARATION OF POLYSTYRENE AT MICA-CYCLOHEXANE INTERFACES. Hiroshi Terashima, Univ. of Tsukuba, Inst. of Materials Sci., Tsukuba, Ibaraki, JAPAN.

The aim of this study is to make a discrimination between the adsorption and the phase separation of polystyrene at mica-cyclohexane interfaces and to discuss a problem about how to identify the adsorption equilibrium. Two experimental approaches have been adopted. The first is the determination of the adsorbance versus time profiles using a Mettler UMT2 ultramicrobalance for polystyrene samples of 1.64, 4.39, 10.7 and  $18.6 \times 10^4$  in molecular weight and at temperatures ranging from 10 to 70°C. The second the observation of polystyrene films floated off from mica to water surface to know the state of surface covering. The adsorption process of polystyrene has been found to consist of two steps, each with its own rate: the initial rapid adsorption and the subsequent slow adsorption. The adsorbance rises rapidly at the beginning and attains to a steady level where the whole surface of mica is completely covered by adsorbed polystyrene molecules. This steady state may be identified with the adsorption equilibrium. The subsequent slow increase in adsorbance has been found to be caused by the adsorption of polystyrene molecules on to the polystyrene films already formed. This fact represents the occurrence of multi-layer adsorption, which is regarded as a beginning of phase separation at the interface. The multi-layer adsorption has been observed for the present samples except for  $1.64 \times 10^4$  at and above the  $\theta$ -temperature.

#### 4:15 PM **\*T6.7**

PHASE TRANSITIONS AND HYSTERESIS IN FLUIDS CONFINED IN NANOPORES. Alexander V. Neimark, Peter Ravikovitch, Aleksey Vishnyakov, TRI/Princeton, Princeton, NJ.

Phase transitions and hysteresis in nanopores are studied by the Monte Carlo simulations and non-local density functional theory. Comparing the theoretical results with the experimental data on capillary condensation of nitrogen and argon in cylindrical channels of the MCM-41 molecular sieves, we have revealed four qualitatively different sorption regimes depending on the temperature and pore size. As the pore size increases at a given temperature or as the temperature decreases at a given pore size, the following regimes are observed consequently: Volume filling without phase separation; Reversible step-wise capillary condensation; Irreversible capillary condensation with developing hysteresis; Capillary condensation with developed hysteresis. We show, that in the regime of developed hysteresis (pores wider than ca.  $\sim 5$  nm in the case of nitrogen sorption at 77K), condensation occurs spontaneously at the vapor-like spinodal while desorption takes place at the equilibrium. Quantitative agreement is found between the modeling results and the experimental hysteresis loops formed by the adsorption-desorption isotherms. The results obtained provide a better understanding of the

general behavior of confined fluids and the specifics of sorption and phase transitions in nanomaterials.

#### 4:45 PM **T6.8**

WHAT HAPPENS IN THE INTERFACE BETWEEN A SILICON RUBBER AND A SILICON OXIDE SURFACE - A CHEMIST'S VIEW. Gun Young Choi, Abraham Ulman, Yitzhak Shnidman, Walter Zurawsky, Polytechnic University, Department of Chemical Engineering and Chemistry, Brooklyn, NY; The NSF MRSEC for Polymers at Engineered Interfaces.

When poly(dimethylsiloxane) (PDMS) cross-linked networks come into contact with a silicon oxide surface, an increase in adhesion hysteresis is observed in the order of increasing molecular weight between cross-links, with a scaling factor of  $\Omega$ . The underlying mechanism of interfacial H-bonds formation has been studied using self-assembled monolayer (SAM) surfaces, and confirmed by studies of isotope effect. An increase in adhesion strength was observed in the order of increasing acidity and number of surface OH groups. As a result of strong interfacial interactions, a thin layer of polymer network with higher elastic constant is formed. Studies of core-shell elastomer systems provide support for this conjecture.

SESSION T7: POSTER SESSION  
Chairs: J. Klafter and Michael Urbakh  
Wednesday Evening, November 29, 2000  
8:00 PM  
Exhibition Hall D (Hynes)

#### **T7.1**

MODELS FOR ELECTROKINETIC PHENOMENA IN CLAYS. Virginie Marry, Jean-Francois Dufrêche, Olivier Bernard and Pierre Turq, Université Pierre et Marie Curie, Paris, FRANCE.

Clays present remarkable electrokinetic features since they exist from very dilute colloidal state to nanoporous compact materials, according to the ratio water/clay. The case of very low volume fraction  $j = V_{\text{water}} / V_{\text{tot}}$  corresponds to compact systems for which the microchannels containing water can either remain as separated entities with a diameter of few nanometers, or coalesce forming channels of larger diameters in smaller number. Obviously any intermediate situation can be encountered. The different ionic distributions corresponding with each of the above situations have been evaluated by Poisson-Boltzmann like models and in some cases compared to Monte-Carlo results. The main electrokinetic properties ( $z$  and streaming potentials, electric conductance) have been evaluated from those values and compared to existing experimental data.

#### **T7.2**

STRUCTURE AND DYNAMICS OF LIQUID CRYSTALS IN SOL-GEL MATRICES. C. Fehr, Groupe de Dynamique des phases Condensées, Université Montpellier II, FRANCE; Ph. Dieudonne, European Synchrotron Radiation Facility (ESRF), FRANCE; C. Goze, Groupe de Dynamique des phases Condensées, Université Montpellier II, FRANCE; Ph. Gaveau, Laboratoire de Physicochimie de la Matière Condensée Université Montpellier II, FRANCE; E. Anglaret, J.L. Sauvajol, Groupe de Dynamique des phases Condensées, Université Montpellier II, FRANCE.

A large amount of work has been carried out in order to understand the effect of confinement on the physical and thermo-dynamical properties of fluids. This is a relevant challenge for many industrial problems and many questions remains open as well on academic point of view. Liquid crystals are model systems to test the effect of confinement due to their original and rich phase diagrams. The orientational and translational orders as well as the dynamics of the molecules are influenced both by confinement and surface interactions. The goal of this work is to study the influence of confinement in the properties of 5CB and 8CB thermotropic liquid crystals in the range of temperatures -10 to 45 degrees. The liquid crystals were confined to sol-gel porous matrices with different pore diameter distributions and different specific areas (Silica Xerogels, Xeroaerogels and Aerogels). The structure and dynamics of those confined liquid crystals were studied by Neutron scattering, Raman polarized spectroscopy and Nuclear Magnetic Resonance. We discuss the effect of the pore size distribution and specific area on the properties of Liquid crystals. We specially (i) Present an interpretation of Carbon-13 NMR spectra which allows to probe the orientational order and the molecule dynamics. (ii) Evidence, by means of Raman and neutron scattering, the coexistence of two solid phases at low temperature for samples quenched from the isotropic phase.

#### **T7.3**

FORCED WETTING OF FLUIDS ON POLYMERIC FIBERS. E. Shim, College of Textiles, North Carolina State University, Raleigh,

NC; Mohan Srinivasarao, School of Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA.

The understanding of wetting phenomena on cylindrically symmetrical objects is very important for spin finish application in fiber/textile industry. Even when a solution easily wets a flat surface, it tends to breakup into droplets on fiber surface due to the extra curvature. The extent of instability is dependent on various factors such as the fiber dimension, fiber surface roughness/geometry, fiber surface energy, surface tension as well as the viscosity of the liquids to be coated, and the processing conditions of the finish application. When a fiber is withdrawn through a liquid reservoir, the liquid film that initially wetted the fiber surface may remain stable or break into droplets. These phenomena can be considered in 3 different stages: dynamic wetting, film formation and film instability development. Dynamic wetting of liquid on Polypropylene (PP) fiber was investigated with a series of glycerol/water solutions and a polymer solution having different viscosity and surface tension. Since PP fibers have lower surface energy than the fluids, these systems were nonwetting and the liquid films broke into droplets immediately after the wetted fibers emerged from the liquid reservoir. The initial film thickness and development of the instability have been investigated on various fibers with liquid having various viscosity and surface tension. The initial film thickness was shown to be a function of capillary number,  $Ca$ , which is defined as the ratio of the viscous to surface tension forces. At low velocity, the initial film thickness followed the LLD (Landau-Levich-Deryaguin) law even though we were dealing with nonwetting systems. Deviations from the LLD law and the instability leading to beading up of the initial fluid film will be discussed.

#### **T7.4**

**UPTAKE OF DNA INTO THE CELL NUCLEUS STUDIED BY SINGLE-MOLECULE MANIPULATION.** Hanna Salman, David Zbaida, Yitzhak Rabin, Didier Chatenay, Michael Elbaum, Weizmann Inst of Science, Dept of Materials and Interfaces, Rehovot, ISRAEL.

The nucleus in eukaryotic cells is delimited by an envelope consisting of concentric lipid bilayer membranes. Molecular traffic of proteins and RNA traverses this boundary through channels known as "nuclear pore complexes" (NPCs), as part of the regulated process of translating the genetic code into functional protein chemistry. The uptake of DNA through the NPCs, while not obviously physiological, lies at the basis of many types of viral infection, as well as proposed modes of genetic therapy, yet little is known about the process. From a physical point of view it is essentially the problem of passing a long and perhaps twisted polymer through a narrow channel. We approach this question experimentally, exploiting techniques of single-molecule manipulation and an in vitro, cell-free nuclear reconstitution system based on amphibian egg extracts. The latter provides intact nuclei in a solution containing a complete cellular biochemistry but lacking the membrane and filamentous structures. Micron-sized latex beads are linked to one or a few molecules of lambda phage DNA, whose distal end may also be labeled by proteins carrying a specific peptide sequence that induces nuclear translocation. These constructs are mixed with the nuclei and transferred to a microscope equipped with optical tweezers. Beads lying nearby the nuclei are selected and drawn away. The distance to which the DNA can be stretched from the nucleus indicates the length of the free molecule remaining outside. By repeating the measurements in time, we access the kinetics of its nuclear uptake. Intriguingly, the rate decreases as the length remaining shortens. Stretching the DNA to a fractional extension is sufficient to stall the shortening, indicating the involvement of sub-picoNewton forces. We interpret the results in a model based on linear diffusion across the pore followed by irreversible retention inside the nucleus.

#### **T7.5**

**ANOMALOUS CARBON DIOXIDE-INDUCED SWELLING OF POLYMER THIN FILMS AT SUPERCRITICAL-GAS PHASE TRANSITION POINTS.** T. Koga<sup>1</sup>, K. Shin<sup>2</sup>, Y. Zhang<sup>2</sup>, Y. Seo<sup>2</sup>, R. Occhiogrosso<sup>3</sup>, M. Rafailovich<sup>2</sup>, J. Sokolov<sup>2</sup>, S. Satija<sup>4</sup>, B. Chu<sup>1</sup>.  
<sup>1</sup>Dept of Chemistry, SUNY at Stony Brook, NY. <sup>2</sup>Dept of MS&E, SUNY at Stony Brook, NY. <sup>3</sup>Bay Shore High School, Bay Shore, NY. <sup>4</sup>Polymer Division and Center for Neutron Research, NIST, Gaithersburg, MD.

The swelling behavior of deuterated polystyrene (d-PS) thin films in contact with carbon dioxide (CO<sub>2</sub>) was monitored by means of in-situ neutron reflectivity. The film thickness of the d-PS monolayer at three different isothermal processes (T=20, 36, 50°C), which are below, just above, further above the critical temperature of carbon dioxide (T<sub>C</sub>=31°C), were determined as a function of pressure ranging from 1 to 750 bar. The pressure dependence of the film thickness above T<sub>C</sub> showed a rapid increase up to 25% approaching the phase boundary between gas and supercritical state, P<sub>ts</sub>. The film thickness is then reduced at high pressure. Such a swelling maximum at P<sub>ts</sub> has never been seen in bulk PS-CO<sub>2</sub> mixtures. In addition, as a result of an isobaric

experiment at 79 bar, the same swelling behavior did not appear at the phase boundary between liquid and supercritical CO<sub>2</sub> phase. Therefore, the anomalous swelling behavior was found to be caused by critical phenomena of pure CO<sub>2</sub>. Surprisingly, in case of rubbery materials, such as deuterated styrene-butadiene copolymer (d-SBR), deuterated polybutadiene (d-PB), the maximum change in thickness was more than by a factor of 2 at P<sub>ts</sub>. This work was funded in part of the NSF-MRSEC program.

#### **T7.6**

**SIMULATION OF GAS SPECIES ADSORPTION IN PACKED BEDS OF POROUS PARTICLES.** Louis J. Piscitelle, Ronald Segars, US Army SBCCOM Natick Soldier Center, Natick, MA.

Continuum models for flow in packed beds of adsorptive particles result in partial differential equations for the effluent concentration. Experimental data [1], show variations in effluent concentrations, for well-controlled input conditions, that cannot be predicted by these deterministic models. Computer simulations based on probability/percolation theories exhibit effluent concentration curves with the same general shape found in the data and predicted by the models, but in addition give bounds on the expected deviations resulting from uncontrollable variations in interstitial pathways. Two approaches to simulate this phenomenon were used. The first method modeled the adsorptive assembly as a collection of flow paths connecting the input to the output reservoirs. The path lengths reflected the number of adsorptive sites encountered along a given physical path through the material. A random number generator selected the number of adsorptive sites along a path. The second method used the Swarm simulation research environment developed at the Santa Fe Institute. In a modified version of the Heatbug simulation, the agents (which represent contaminants in the flow) are moving in a globally structured, heterogeneous environment consisting of staggered columns of islands which can trap the agents. While there is a net flow of the agents, each individual agent has a random perturbation applied to this mean motion. Both methods result in sigmoidal output concentration profiles and in the Swarm simulation the spatial concentration gradient is also calculated. These results agree qualitatively with previous experimental and theoretical results and allow a mechanism for explaining the observed random variations. 1. D. Rivin, C.E. Kendrick, Private Communication.

#### **T7.7**

**SURFACE AND VOLUME DIFFUSION OF WATER AND OIL IN POROUS MEDIA BY FIELD CYCLING NUCLEAR RELAXATION AND PGSE NMR.** Sophie Godefroy, Jean-Pierre Korb, Dominique Petit, Laboratoire de Physique de la Matière Condensée, UMR 7643 CNRS, École Polytechnique, Palaiseau, FRANCE; Marc Fleury, Institut Français du Pétrole, Reuil-Malmaison, FRANCE; Robert G. Bryant, Department of Chemistry, University of Virginia, Charlottesville, VA.

Low field NMR provides critical information on porous media, such as porosity, permeability, saturation, pore size distribution and wettability. Its use in well logging allows relevant evaluations of oilfields. However, a pertinent use requires the understanding of the molecular dynamics at the surface of the pore. Here we propose an original method to probe the microdynamics of water and oil at the pore surface. Different NMR techniques allow a measurement of the surface and volume diffusion coefficients of water and oil in pores. To study the role of liquid-solid interfaces that are commonly found in oilfields, we use packing of calibrated grains of SiC (partly covered by silica), packing of calcite grains and natural rocks of sandstone and limestone. These porous media were fully saturated with water or oil. We have measured nuclear relaxation times of protons (T<sub>1</sub> and T<sub>2</sub>) at 2 MHz and different temperatures. T<sub>1</sub> was also measured at frequencies varying between 0.01 and 25 MHz, using the field cycling NMR technique, for different temperatures. Diffusion measurements were performed by Pulsed Gradient Spin-Echo (PGSE) NMR technique. Varying the magnetic field and the temperature allows us to evidence a surface diffusion of the proton species limited by the exchange with the bulk population. The temperature behavior of the relaxation times is different for SiO<sub>2</sub> and CaCO<sub>3</sub> surfaces, which has important applications for NMR well logging. Surface diffusion coefficients measured by field cycling were found to be an order of magnitude lower than that measured by PGSE NMR. All these combined NMR techniques allow us to precise the relation between relaxation times and pore sizes.

#### **T7.8**

**CAYLEY TREE RANDOM WALK DYNAMICS.** D. Katsoulis, P. Argyrakis, University of Thessaloniki, Department of Physics, Thessaloniki, GREECE; A. Pimenov and A. Vitukhnovsky, P.N. Lebedev Physics Institute RAS, Lebedev Research Center in Physics, Moscow, RUSSIA.

We investigate diffusion on newly synthesized dendrimer structures.

We focus on the mean square displacement of the diffusing particles, and the area probed, as given by the walk parameter  $S(N)$ , the number of the distinct sites visited, on different coordination number,  $z$ , and different generation number  $g$  of a dendrimer structure as modeled by a Cayley tree. We simulate the trapping kinetics curves for these structures and compare the finite and the infinite cases, and also with the cases of regular dimensionality lattices. We construct the Cayley tree lattice with the given coordination number  $z$  ( $z=2,3,4,5$ ). We modeled trees with  $g$  larger than 1000000, which was more than the length of the random walk monitored. The minimum number of hops a walker should perform to get from one site to another defines the distance between nodes. In order to simulate the trapping process we designated a small part (ca.10<sup>-3</sup>) of the nodes as traps. When a particle reaches a trap it is irreversibly trapped, and the time to trapping was recorded. We find that the movement of the walker is strongly biased towards the periphery. For small dendrimer structures,  $S(N)$  approaches the overall number of the dendrimer nodes, while for the infinite tree it grows linearly with time. The average displacement behaves the same way. For finite dendrimers it stabilizes in the range ( $g-2g$ ) and for infinite ones it grows to infinity. The rate of growth of these numbers is a function of  $z$ , and the higher the  $z$  the faster these quantities grow. The trapping intensity curves for the infinite Cayley tree should be monoexponential curves. Here we expect a very complex decay profile, which, to a first approximation could be treated as two-exponential decay: the first exponential corresponding to the fast decay with the rate equal to the infinite case, while the second exponent would be a decay characterized by a decay time several orders higher. Acknowledgements: This work was supported by NATO grant SFP97-1940.

### **T7.9**

**THE ROLE OF DIELECTRIC RELAXATION IN ELECTRO-RHEOLOGY IN DC ELECTRIC FIELDS.** Ujitha Dassanayake, Brandeis Univ, Dept of Physics, Waltham, MA; Yue Hu, Wellesley College, Dept of Physics, Wellesley, MA.

When a large electric field is applied to a suspension of small particles in an insulating fluid, the viscosity of the suspension can increase drastically from the value in the absence of a field. Despite its great application potential, the mechanism responsible for this electrorheological (ER) effect has been poorly understood. Traditionally, ER effects have been considered to arise from the dipole-dipole interactions between the polarized particles, with the strength of the dipole moment determined by the conductive mismatch between the fluid and the particles in DC fields. Experimental results have shown that the dielectric relaxation frequency plays an important role in ER effects. We have investigated ER effects using computer simulation. The polarization of the particles is affected by the spinning motion of the particles under shear, causing a misalignment between the dipole moment and the applied electric field. We have found an optimal dielectric relaxation frequency at high shear rates, in qualitative agreement with experimental observations.

Work supported by the Department of Energy (grant no. DE-FG02-94ER45522).

### **T7.10**

**THERMODYNAMICS AND KINETICS OF SHEAR INDUCED MELTING OF A THIN LUBRICATION FILM TRAPPED BETWEEN SOLIDS.** Valentin L. Popov, University of Paderborn, GERMANY; B.N.J. Persson, IFF, FZ Jülich, Jülich, GERMANY.

The behavior of a thin lubrication layer is described in a model combining the Landau theory of phase transformations and the Frenkel-Kontorova model. The kinetic equation for the shear modulus is obtained and solved together with the equation of overdamped motion of the layer. The maximum static and the minimum kinetic friction stresses as well as the dependence of kinetic friction stress on sliding velocity are calculated analytically. The state of the layer during sliding is determined by a dimensionless parameter  $\gamma$ . At small values of  $\gamma$  shearing of the layer causes its melting. For large values of  $\gamma$  no shear melting occurs: the stable state is that of solid-state sliding. The transition from static to kinetic friction occurs in an interval of extremely small velocities defined as ratio of the lattice parameter to the relaxation time of the shear modulus.

### **T7.11**

**GEL-FREE EXPERIMENTS OF REACTION FRONT KINETICS IN CONFINED GEOMETRY.** Sung Hyun Park, Steve Parus, Raoul Kopelman, University of Michigan, Department of Chemistry, Ann Arbor, MI; Haim Taitelbaum, Bar-Ilan University, Department of Physics, Ramat-Gan, ISRAEL.

We present a new experimental system to study the kinetics of the reaction front in the  $A + B \rightarrow C$  reaction-diffusion system with initially separated reactants. The system composed of a CCD camera monitoring the kinetics of the front formed in the reaction-diffusion

system  $Cu^{2+}$  tetra  $\rightarrow$  1:1 complex (in aqueous, gel-free solution) inside a 75  $\mu m$  gap between two flat microscope slides. This is basically a two-dimensional system. The use of gel-free solution inside small confined geometry is very promising with respect to more controlled investigation of the kinetics of reaction front under non-convection environment. The results agree with the theoretical predictions for the anomalous time dependence of the front's width, height, and location.

### **T7.12**

**THERMAL STABILITY AND DYNAMICS IN THIN POLY-CARBONATE FILMS.** Christopher L. Soles<sup>1</sup>, Robert M. Dimeo<sup>2</sup>, Eric K. Lin<sup>1</sup>, Jack F. Douglas<sup>1</sup> and Wen-li Wu<sup>1</sup>, NIST. <sup>1</sup>Polymers Division, <sup>2</sup>Center for Neutron Research, Gaithersburg, MD.

Recently there has been a wealth of experimental and theoretical works addressing the deviations from bulk-like behavior that can arise when a polymer is constrained in a thin film. Of particular interest are the various confinement-induced shifts in the apparent glass transition temperature that are reported in the literature and what these shifts imply about the polymers dynamics. The techniques used to monitor such shifts in the apparent glass transition typically do not monitor the dynamics directly, rather rely upon inferences from related quantities such as film thickness or index of refraction. In this work, we examine as a function of thickness and temperature a series of polycarbonate films supported on silicon wafers. An apparent glass transition is obtained by monitoring the film thickness as a function of temperature using specular X-ray reflectivity. Films thicker than 100  $\text{\AA}$  were found to be very bulk-like in their expansion behavior and apparent glass transition temperature. However, a suppression of the apparent glass transition temperature is observed in the sub-100  $\text{\AA}$  films. Furthermore, a negative coefficient of thermal expansion is encountered in these sub-100  $\text{\AA}$  films well below the apparent glass transition temperature. To better understand this unexpected behavior, the polymer dynamics of the thin films are monitored directly with the high resolution High Flux Backscattering Spectrometer at the NIST Center for Neutron Research. Fixed-window elastic energy scans as a function of temperature on stacks of multiple wafers/films allow one to monitor the decrease in the elastically scattered neutrons as a function of  $Q$ , and thus determine the mean-square-displacement of the hydrogenous polymer segments through the Debye-Waller factor. To the best of our knowledge, this is the first time that the dynamics of a thin polymer film have been directly observed using neutron scattering techniques.

### **T7.13**

**TEMPERATURE-DEPENDENT GROWTH MECHANISMS OF OCTADECYLPHOSPHONIC ACID ON SAPPHIRE.** Christian Messerschmidt, Daniel K. Schwartz, Tulane Univ, Dept of Chemistry, New Orleans, LA.

We investigated the monolayer growth of octadecylphosphonic acid on sapphire at different temperatures using atomic force microscopy (AFM) and contact angle measurements. At room temperature a continuous layer forms, from which islands of higher order grow. At lower temperatures, however, growth proceeds via island nucleation on the bare substrate. At intermediate temperatures both growth modes can be found coexisting on the same sample. These findings can be interpreted in terms of a 2D-phase diagram. Depending on the temperature the growing monolayer will reach the solid phase via the liquid phase or, if the temperature is below the triple point, directly from the gaseous phase. In the latter case, bare sapphire is still exposed during growth, detectable by significantly lower contact angles, while the surface is covered by the liquid phase at higher temperatures. Different crystal faces of sapphire (C- and R-sapphire respectively) showed different growth kinetics, detectable by AFM height imaging and hexadecane contact angles. The unavoidable step edges found on sapphire, which are due to miscut of the wafer, have an influence on growth. On samples where both growth modes are detectable the liquid phase has a preference for the edges whereas island growth favors the terraces.

### **T7.14**

**ADSORPTION/CONDENSATION OF RARE GASES IN SILICA CONTROLLED POROUS GLASS: A GRAND CANONICAL MONTE-CARLO STUDY.** Roland J-M Pellenq and Pierre Levitz Centre de Recherche sur la Matière Divisée CNRS et Université d'Orléans, Orléans, FRANCE.

We have studied adsorption of argon, krypton and xenon in a mesoporous silica Controlled Porous Glass (CPG) by means of Grand Canonical Monte-Carlo (GCMC) simulation. Several numerical samples of the CPG adsorbent have been obtained by using an off-lattice reconstruction method recently introduced to reproduce topological and morphological properties of correlated disordered porous materials [1]. The off-lattice functional of Vycor is applied to a simulation box containing silicon and oxygen atoms of cubic cristoballite with an homothetic reduction of factor 2.5 so to obtain

30A-CPG sample. The off-lattice functional represents the volume autocorrelation function of the porous structure as determined from TEM image analysis. It allows to cut out portion of the initial volume in order to create the porosity. A realistic surface chemistry is then obtained by saturating all oxygen dangling bonds with hydrogen. All numerical samples have statistically the same structural properties as revealed from small angle spectra analysis [2]. The adsorbate (Ar, Kr, Xe) /adsorbent potential functions as used in GCMC simulations, are derived from the PN model [3]. Adsorption isotherms are calculated for each sample. These are of type IV or V: they exhibit a capillary condensation transition but with a finite slope by contrast to that obtained in simple geometries such as slits and cylinders. Simulated isotherms are in good agreement with experiment. The analysis of the adsorbed density reveals that the adsorption mechanism for argon (at 77 K) differs from that for xenon (at 195 K): Ar forms a thin layer which covers all the surface prior to condensation while Xe condensates in the higher surface curvature regions without forming a continuous film. This is interpreted on the basis of the Zisman law for wetting: it is based on a contrast of polarizability between the adsorbate and the atoms of the adsorbent. The difference of behavior upon adsorption has important implications for the characterization of porous material by means of physical adsorption. The adsorption/desorption data for argon at several temperatures allow to calculate a coexistence curve which shows that the critical temperature of the confined fluid is decreased by 15 K compared to that of the bulk. [1] P. Levitz, *Adv. Coll. and Interf. Sci.*, 1998, 76, p 71. [2] R.J.M. Pellenq, S. Rodts, V. Pasquier, A. Delville, P. Levitz, *Adsorption*, 2000, in press. [3] R.J.M. Pellenq, D. Nicholson, *J. Phys. Chem.*, 1994, 98, p 13339.

#### **T7.15**

**HYDROCARBON REACTIONS IN CARBON NANOTUBES: PYROLYSIS.** Steven J. Stuart, Bradley M. Dickson, Clemson University, Clemson, SC; Bobby G. Sumpter, Donald W. Noid, Oak Ridge National Laboratory, Chemistry Division, Oak Ridge, TN.

Carbon nanotubes have been used as nanoscale reaction vessels for a variety of aqueous solutions and metallic compounds. So far they have not been widely utilized for organic species. In this study, we use molecular dynamics simulations to investigate the thermal decomposition of linear alkanes absorbed in carbon nanotubes. The reactive molecular dynamics simulations are performed with the newly developed AIREBO (adaptive intermolecular reactive empirical bond-order) model, which enables accurate treatment of both nonbonded interactions and covalent bond formation/dissociation. Pyrolysis when confined to a nanotube is compared to pyrolysis in the gas phase using this model. Both reactions exhibit the expected first-order kinetics, with the decomposition proceeding faster in vacuum than in the nanotube by approximately 40%. Minor differences in product distributions are also observed.

#### **T7.16**

**DEPOSITION OF LIQUID MICRO-STRUCTURES ON CHEMICALLY PATTERNED SURFACES.** Anton A. Darhuber, Sandra M. Trojan, Jeffrey M. Davis, Scott M. Miller, Princeton Univ, Dept of Chemical Engineering, Princeton, NJ; Sigurd Wagner, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ.

Many microelectronic and bioengineering applications stand to benefit from the miniaturization of liquid deposition onto chemically heterogeneous surfaces. The liquid confinement, enforced by differences in surface energy, serves to provide large area arrays for chemical microreactors or genetic analysis. Industrial interest in creating large-scale liquid arrays in a rapid and cheap fashion has mainly focused on pin tool or ink-jet droplet deposition. For the applications cited, the liquid placement and volume deposited must be reproducible and precise. We report on a theoretical and experimental study of dip-coating and meniscus coating as a simple, reliable and accurate technique for controlled deposition of liquid patterns with feature sizes in the micron range. Silanized silicon or glass substrates with hydrophilic regions of various shapes and dimensions are coated at low capillary number to produce minimal-surface liquid multi-arrays. The two key challenges of this study are (a) the creation of liquid distributions of uniform height, irrespective of pattern geometry, orientation and density, and (b) the prediction of the deposited volume as a function of material and process parameters. Besides the interplay between capillary and viscous forces, which are controlled by the liquid surface tension, viscosity and the coating speed, our studies reveal "interference effects" caused by the pattern shape and density, as reflected for instance by the ratio of hydrophilic to hydrophobic surface area. Our theoretical prediction of the maximum film height deposited on elementary geometric shapes like hydrophilic lines is in excellent agreement with experiment. Because the imposed surface patterns induce characteristic length scales much smaller than the capillary length, the correlation between the film thickness and the capillary number deviates substantially from the classical Landau-Levich result.

#### **T7.17**

**SUPRAMOLECULAR ASSEMBLY OF SOME METAL IONS WITH S-AND N-PENDANT LIGANDS OF SUBSTITUTED 2,2'-BIPYRIDINE.** B.K. Kanungo, Minati Baral, Sant Longowal Institute of Engineering and Technology, Department of Chemistry, Longowal, Punjab, INDIA; Peter Moore, University of Warwick, Department of Chemistry, Coventry, UNITED KINGDOM.

There has been considerable increase of the use of 2,2'-bipyridine (bipy) and substituted bipyridine ligands in the past two decades, simulated by the attractive photochemical and photophysical properties exhibited by the ligands and some of their metal complexes. In this study, three potentially quadridentate ligands (L1-L3) which bear two bipy arms, have been synthesised and characterised. The spacer group in the ligands allows both bipyridyl groups to coordinate to the same metal ion, to give tetrahedral complexes with d10 metal ions [Cu(I), Ag(I)], and six coordinate complexes of the type cis-[ML<sub>4</sub>X<sub>2</sub>]<sub>n</sub> with other transition metals [e.g. Fe(II), Ru(II), Ni(II)]. The considerable stability of these cis-complexes makes them potentially useful as Lewis acid catalysts. The ligand 1,4,7-tris(2,2'-bipyridyl-5-ylmethyl)-,4,7-triazacyclononane (I) forms very stable 1:1 mononuclear complexes with di- and tri-valent metal ions by coordination of all three pendant bipy groups. Synthesis of a similar ligand (L4) was made by reacting TAMCH with three equivalent of 5-bromomethyl-2,2'-bipyridine. The ligands and their metal complexes with some transition metal ions were synthesised and characterized by NMR, UV-visible, mass and infrared spectra, and by analytical data. The molecular modelling study, synthetic method, structural characterization of the ligands and metal complexes will be discussed.

#### **T7.18**

**FORCED WETTING OF COMPLEX FLUIDS ON CYLINDRICAL OBJECTS.** Jung Ok Park, Mohan Srinivasarao, and A.D. Rey.

In many industrial applications it is necessary to coat a solid substrate with a fluid. This is usually accomplished by dragging the solid object through the fluid of interest. Here we refer to such processes as forced wetting of the solid substrate, irrespective of whether the fluid is a wetting or a nonwetting fluid for the substrate. In such a process it is obvious that the thickness of the fluid coating will depend on the velocity at which the solid substrate is withdrawn. At zero velocity the film thickness is zero (where we ignore the possibility of a thin wetting film) and at infinite velocity it will be zero as well, since the fluid does not have enough time to form a coating. Thus a maximum wetting speed naturally enters the problem of forced wetting, as has been discussed in the literature. In this talk we are interested in addressing the issue of forced wetting of fluids where the fluids are complex fluids. In particular, we confine our attention to the special case of the solid substrate having a cylindrical geometry and where the fluid is an anisotropic fluid with long range orientational order. We consider the case of a nematic fluid and a polymer solution whose concentration is above the overlap concentration being coated onto a polypropylene fiber. In both cases the initial thickness of the fluid film coated on the fiber is proportional to the capillary number, Ca (defined as the ratio of the viscous forces to those due to surface tension), to the first power. We present a model to account for the observed thickness dependence on the capillary number.

#### **T7.19**

**MOLECULAR DYNAMICS AND RELAXATION METHODS IN THE STABILITY CALCULATIONS FOR THE STUDY OF DISTORTIONS OF CONFINED NEMATIC LIQUID CRYSTALS.** A. Calles, R.M. Valladares, J.J. Castro, Faculty of Sciences, National University of Mexico, MEXICO.

We present a comparison of molecular dynamics and relaxation methods simulations for the study of the orientational ordering of a nematic liquid crystal near the surface confining the system, in 2D and 3D. The system is simulated through a lattice model with a superposition of isotropic and anisotropic intermolecular interactions of the Maier-Saupe and induce dipole-induce dipole type force for the bulk nematic phase. For the nematic confining surface we consider a Rapini-Papoular interaction.

#### **T7.20**

**EVIDENCE FOR ATTRACTIVE POTENTIALS BETWEEN PROTEINS, MEDIATED BY BILAYERS FLUCTUATIONS.** Nicolas Taulier, Faculty of Pharmacy, University of Toronto, Ontario, CANADA; Marcel Waks, Marcel Gindre, Laboratoire d'imagerie parametrique, Paris, FRANCE; Wladimir Urbach, Laboratoire de Physique Statistique de l'Ecole Normale Supérieure, Paris, FRANCE.

We have investigated the distribution of the myelin transmembrane protein after insertion into an oil-swollen lamellar phase of hydrophobic thickness D. When  $D > d_p$ , the hydrophobic length of

the protein  $\alpha$ -helices, sole repulsive interactions are found between proteins. The repulsive force is of electrostatic nature, arising from charges borne by the protein. When  $D < d_{\pi}$ , an attractive force is observed in addition to the repulsive interaction. The attractive interaction potential between proteins, deduced from digitized freeze-fracture micrographs, is in excellent agreements with the model of membrane-mediated interactions, originating from the thermal undulations of lamellae.

#### **T7.21**

**COVALENTLY BOUND MOLECULAR LAYERS ON TRANSPARENT SILICA AND GOLD SUBSTRATES FOR SURFACE FORCE MEASUREMENTS.** Marina Ruths, Diethelm Johannsmann, Jürgen Rühle, Wolfgang Knoll, Max-Planck-Institute for Polymer Research, Mainz, GERMANY; Manfred Heuberger, ETH Zurich, SWITZERLAND.

We demonstrate the use of reactive substrates in interferometric surface force measurements by studying (a) polystyrene brushes formed by radical chain polymerization from azomono-chlorosilane initiator monolayers on thin quartz-glass sheets, and (b) self-assembled alkanethiol monolayers on transparent, continuous gold layers evaporated on mica.

#### **T7.22**

**THE INFLUENCE OF BOUNDARY CONDITIONS AND SURFACE LAYER THICKNESS ON DIELECTRIC RELAXATION OF LIQUID CRYSTALS CONFINED IN CYLINDRICAL PORES.** Zaira Nazario, Fouad Aliev, Department of Physics, University of Puerto Rico, San Juan, PR; Ghanshyam Sinha, Department of Physics, CWRU, Cleveland, OH.

Dielectric spectroscopy was applied to investigate the dynamic properties of liquid crystals alkylcyanobiphenyls (5CB and 8CB) confined in 2000 Å cylindrical pores of Anopore membranes with axial (planar) and homeotropic boundary conditions on the pore walls. Homeotropic boundary conditions of confined 5CB and 8CB allow the investigation of the librational mode in these LCs by dielectric spectroscopy since the probing electric field is parallel to the pore axis. We found that the dynamics of the librational mode is totally different from the behavior observed in investigations of relaxation due to reorientation of molecules around their short axis. First of all the frequency corresponding to the maximum in the spectrum of the imaginary part of dielectric permittivity, is more than one order of magnitude greater for librational mode. The spectra are wider and the asymmetry in the spectra is greater in the homeotropic alignment than in the axial orientation. The interpretation of the temperature dependencies of relaxation times and of the dielectric strength needs the involvement of the temperature dependence of orientational order parameter. Layers of different thickness were formed on the pore walls as a result of controlled impregnation of porous matrices with 8CB from solutions of different liquid crystal concentration. The process due to rotation of molecules around their short axis with single relaxation time observed for bulk 8CB is replaced by process with a distribution of relaxation times in thin layers. The main relaxation process broadens with decreasing thickness. The magnitudes and the temperature dependence of the relaxation times of the process due to the rotation of molecules around their short axis as well as nematic-isotropic phase transition temperatures were very sensitive to the thickness layer. These experiments allow the clarification of the role of surface layers on the physical properties of geometrically restricted LC.

#### **T7.23**

**THE STRETCHING AND REFOLDING OF THE  $\alpha$ -HELIX FORM OF A PEPTIDE SINGLE MOLECULE USING MAGNETIC FORCE CONTROLLED AFM.** Masami Kageshima, Mark A. Lantz<sup>a</sup>, JRCAT-ATP, Tsukuba, JAPAN; Seiji Takeda, Arkadiusz Ptak, Chikashi Nakamura, Jun Miyake, NAIR, Tsukuba, JAPAN; Suzanne P. Jarvis, Hiroshi Tokumoto, JRCAT-NAIR, Tsukuba, JAPAN; (<sup>a</sup> present address: Inst. of Physics, Univ. of Basel).

The  $\alpha$ -helix form of a cysteine<sub>3</sub>-lysine<sub>30</sub>-cysteine (C<sub>3</sub>K<sub>30</sub>C) peptide single molecule was stretched while both the applied force and the stiffness of the molecule were measured with a magnetic-force-controlled AFM technique in liquid. The end of the molecule with one cysteine residue was captured with a gold-coated AFM tip and stretched while the other end was bonded onto the gold substrate with three Au-S bonds. The stiffness was measured directly by driving the cantilever with an extremely small sinusoidal magnetic force less than 5 pN, via a magnet particle mounted on the backside of the cantilever. Both the force and stiffness were recorded until the bonding between the molecule and the tip ruptured. The total work done by the cantilever on the molecule was evaluated from the applied force and the elongation length, hence the energy required to break one hydrogen bond in the helix was calculated. In a solution of pH=10.5, this energy was significantly larger than the reported typical hydrogen

bond energy in water [1]. Note that the present result might be an overestimate because it contains contribution from the deformation energy of the helix backbone or energy dissipation by abrupt relaxation of the cantilever at the breaking points of the hydrogen bonds. For comparison, control measurements were also made in solution with different pH values in which the hydrogen bonds in polylysine are less effective. In addition to the stretching experiment, the tip-sample separation was reversed before rupturing in order to investigate the refolding process of the molecule. The results of this experiment will also be presented. [1] A.R. Rees and M.J.E. Sternberg, From Cells to Atoms (Blackwell Scientific Publications, Oxford, 1984).

#### **T7.24**

**ELECTRONIC AND DIPOLAR EFFECTS IN ADSORPTION KINETICS OF THIOLS ON GOLD.** Shang Liao, Abraham Ulman, Yitzhak Shnidman, Polytechnic University, Brooklyn, NY; The NSF MRSEC for Polymers at Engineered Interfaces.

We present the first experimental evidence that the molecular dipole and the electron density on the S-atom affect the adsorption process of thiols on gold. The adsorption kinetics of five rigid 4-mercaptobiphenyls onto gold surfaces has been studied by the quartz crystal microbalance (QCM) technique. The kinetics data cannot be fitted to the Langmuir equation because it does not take interadsorbate interactions into consideration. A new lattice-gas adsorption model was developed that approximates the chemisorbed layer of interacting mercaptobiphenyls as lattice-gas particles with pair interactions between nearest-neighbor sites. The interacting lattice-gas model produces much better fits to experimental data and provides quantitative estimates of the strength of the chemisorption potential and the dipolar interactions, as well as of the rate constants.

#### **T7.25**

**COMPOSITIONAL DEPENDENCE OF FERROMAGNETIC RESONANCE (FMR) LINEWIDTH IN NICKEL-ZINC FERRITES POLYCRYSTALS.** Hee Bum Hong, Tae Young Byun, Kug Sun Hong, School of MS&E, College of Engineering Seoul National University, Seoul, KOREA.

The systematic variation in linewidth of ferromagnetic resonance (FMR) with the content of Fe was observed at X band (9.78GHz) in the (Ni<sub>0.5</sub>Zn<sub>0.5</sub>)<sub>1-x</sub>Fe<sub>2x</sub>O<sub>4</sub> systems (-0.2 ≤ x ≤ 0.2). The linewidth of the stoichiometric sample (x = 0) had minimum value, 50 Oe. In contrast the linewidth of the Fe non-stoichiometric samples sharply increased to 210 Oe with increasing Fe non-stoichiometry (x). The mechanism for broadening of line width was investigated using thermoelectric power and electrical resistivity, since the contribution of anisotropy and porosity to the linewidth was negligible in all composition range. Fe<sup>2+</sup> ions increased with increasing Fe content which cause a broadening of linewidth due to relaxation, in Fe excess region. But, it was observed that Ni<sup>3+</sup> and Fe<sup>2+</sup> ions coexisted in Fe deficient region. Therefore the increase of linewidth in this study originated from the Fe<sup>2+</sup>/Fe<sup>3+</sup> magnetic relaxation, and the Fe<sup>2+</sup>/Fe<sup>3+</sup>, Ni<sup>2+</sup>/Ni<sup>3+</sup> magnetic relaxation, in Fe excess and Fe deficient region, respectively.

#### **T7.26**

Abstract Withdrawn.

#### **T7.27**

**STUDIES OF TEMPERATURE-DEPENDENT EXCIMER-MONOMER CONVERSION IN A DENDRIMERIC ANTENNA SUPERMOLECULE BY FLUORESCENCE SPECTROSCOPY.** Youfu Cao, Raoul Kopelman, Department of Chemistry, University of Michigan, Ann Arbor, MI.

Nanostar, a phenylacetylene (PA) dendrimer labeled with perylene, is discovered to exhibit temperature-dependent emission spectra in certain organic solvents over the temperature range of 10-65°C. The monomer signal is increasing exponentially with increased temperature, while the excimer signal decreases. Models of excimer formation and dimer dissociation dynamics are included, and the equilibrium constants at different temperature are calculated. This behavior suggests nanostar's potential application in fluorescence-based optical thermometry, which is being investigated.

SESSION T8:

Chair: Gleb Oshanin

Thursday Morning, November 30, 2000  
Room 313 (Hynes)

#### **8:30 AM \*T8.1**

**CONFINED SYSTEMS OF DIBLOCK COPOLYMERS: GRAIN BOUNDARIES AND SURFACE INDUCED ORDERING.** David

Andelman, Yoav Tsori, School of Physics and Astronomy, Tel Aviv University, Tel Aviv, ISRAEL.

Diblock copolymers exhibit a variety of spatially modulated phases as competition between molecular and entropic forces which select a preferred spatial periodicity. In particular, we investigate defects in phases with lamellar symmetry typical of symmetric diblock systems. Grain boundaries are formed in lamellar systems when two lamellar domains of different orientations meet. The form of the interface strongly depends on the angle between the normals of the grains. We present a theoretical approach to find the shape of tilt boundaries in two-dimensional systems, based on a Ginzburg-Landau expansion of the free energy which describes the appearance of lamellae. Close to the tips at which lamellae from different grains meet, these lamellae are distorted. Minimization of the free energy results in a linear fourth order differential equation for the distortion field, with proper constraints, similar to the Mathieu equation. The calculated monomer profile and line tension agree qualitatively with transmission electron microscope experiments, and with full numerical solution of the same problem. Lamellar phases are also studied in the vicinity of flat, chemically patterned surfaces. Above the order-disorder transition the propagation of several surface patterns into the disorder bulk is investigated. The oscillation period and decay length of the surface q-modes are given in terms of the system parameters. We observe lateral order parallel to the surface as a result of order perpendicular to the surface. For a localized surface pattern, lamellar layering occurs far from the surface, but close to it these lamellae are perturbed to adjust to the chemical pattern.

#### 9:00 AM \*T8.2

DIRECT EXPERIMENTAL EVIDENCE OF FLOW WITH SLIP AT SIMPLE LIQUID - SOLID INTERFACES. R. Pit, H. Hervet, L. Leger Laboratoire de Physique de la Matière Condensée, URA CNRS 792, Collège de France, Paris, FRANCE.

The boundary condition for the flow velocity of a Newtonian fluid near a solid wall has been probed experimentally using a novel technique based on total internal reflexion and fluorescence recovery after photobleaching (TIR - FRAP). The resolution in distances from the wall is of the order of 80 nm. For hexadecane flowing on a smooth alumina surface covered with a dense monolayer of octadecyl-trichlorosilane, clear evidence of slip at the wall will be presented, with a slip length of 400 nm. Systematic experiments performed on the same solid, with various surface treatments show that both the strength of the interactions between the liquid and the solid and the surface roughness at molecular scales deeply influence the amount of wall slip and act in antagonist ways. Additional experiments performed on the same surfaces with another simple liquid (squalane) will also be presented, establishing the generality of the observed phenomenon.

#### 9:30 AM T8.3

EXPERIMENTAL EVIDENCE FOR A LARGE SLIP EFFECT AT A NONWETTING FLUID SOLID INTERFACE. E. Charlaix, J. Baudry, D. Mazuyer, A. Tonck, Département de Physique des Matériaux, Université Claude Bernard and CNRS, Villeurbanne Cedex, FRANCE; Laboratoire de Tribologie et Dynamique des Systèmes, UMR CNRS 5513, Ecole Centrale de Lyon, Ecully Cedex, FRANCE.

It is shown that the flow of a simple Newtonian liquid near a hard wall can be affected by the chemical nature of this wall. We have studied with a Surface Force Apparatus (SFA) the hydrodynamic force between a sphere and a plane immersed in glycerol. The drainage of the thin film is different on a hydrophobic plane and a hydrophilic one. This effect can be interpreted, when the film is not too thin, by the existence of a slipping velocity at the boundary between the liquid and the hydrophobic solid. The slipping length is about 65 times the glycerol molecular size.

#### 10:15 AM \*T8.4

ANOMALOUS SURFACE CONFORMATION FOR POLYMERIC GAS-HYDRATE-CRYSTAL INHIBITORS. H.E. King, Jr.; Jeffrey L. Hutter; Min Y. Lin; Thomas Sun, ExxonMobil Research and Engineering Company, Annandale, NJ.

Small-angle neutron scattering was used to characterize the polymer conformations of four non-ionic water soluble polymers: poly(ethylene oxide), poly(N-vinyl-2-pyrrolidone), poly(N-vinyl-2-caprolactam), and an N-methyl, N-vinylacetamide/N-vinyl-2-caprolactam copolymer. The last three of these kinetically suppress hydrate crystallization, and their inhibitor activity ranges from moderate to very effective. This attribute is of significant commercial importance to the oil and gas industry, but the mechanism of the activity is not understood. Our results on polymer conformation in solution shows there to be little difference among the four polymers: the scattering is that expected for a polymer in a good solvent. However, in the presence of

a hydrate-crystal/liquid slurry, the three inhibitor polymers significantly alter their conformation. This arises from a change in polymer conformation on the crystal surfaces. We utilize neutron contrast variation methods to examine this polymer conformation. Unlike the expected de Gennes self-similar structure, as observed in other adsorbed polymer layers, this surface exhibits a polymer layer with a thickness several times the polymer coil dimension. Nevertheless, the polymer coverage is only  $5 \pm 3 \text{ mg/m}^2$ . The structural model which results suggests that polymer clumps cover a small (2%) fraction of the available surface. Therefore, most of the polymer does not bind to the surface, suggesting the formation of surface aggregates. We suggest how these aggregates could affect the growth inhibition of hydrate crystals.

#### 10:45 AM T8.5

EXPLORING HETEROGENEITIES IN ACTIN NETWORKS. M. Gardel, M. Valentine, M. Nikilaides, A.R. Bausch and D.A. Weitz, Harvard University, Department of Physics, Cambridge, MA.

The technique of microrheology is now widely applied to study the microscopic viscoelastic properties of complex fluids, including polymer networks. The thermal motion of single beads embedded in the polymer is used to extract its local viscoelastic moduli. However, comparison of bulk and micro-rheological results exhibit discrepancies, which are thought to be either due to the heterogeneous nature of the network or the coupling of the probe particles to the medium. Here we present results studying actin network, a semiflexible polymer. We use a multiparticle - tracking approach to measure the local heterogeneities of the actin network. In another attempt to understand the heterogeneity of the network, the recently developed technique of two-point microrheology is used. Comparisons between the three different interpretations of the microrheological measurements are made and their further implications will be discussed.

#### 11:00 AM T8.6

FLUCTUATIONS IN SPARSELY POPULATED REACTION SCHEMES: RANDOM TRIGGERING OF THE GENETIC SWITCH? Ralf Metzler and Peter G. Wolynes, Department of Physics and School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, IL.

Single molecule dynamics is but one example where the traditional ensemble averages fail. A similar situation is encountered in the reaction of a small number of chemical reactants. Here, the number fluctuations become relevant, and discrete modelling has to be used instead of differential kinetics equations. For a simplistic reaction scheme, we present analytical results of the associated master equation. Especially, the behaviour of the probability that the number of particles of the species under consideration does not fall short of a certain threshold number is analysed. On the basis of this model, we discuss the question whether fluctuations are strong enough to trigger the genetic switch in a cellular gene regulation cycle, i.e., to determine whether a specified external signal is needed to terminate a certain cellular, "stable" state, or whether fluctuations actually may play a significant role in the fate of a living cell.

#### 11:15 AM \*T8.7

POLYMERS IN CONFINING GEOMETRIES: FROM ISOLATED POLYMER CHAINS TO POLYMER BRUSHES. F. Kremer, L. Hartmann, A. Huwe, Th. Kratzmüller<sup>a</sup>, H.G. Braun<sup>a</sup>, A. Gräser<sup>b</sup>, S. Spange<sup>b</sup>, Universität Leipzig, Fakultät für Physik und Geowissenschaften, Leipzig, GERMANY; <sup>a</sup>Institut für Polymerforschung, Dresden, GERMANY; <sup>b</sup>Technische Universität Chemnitz, Chemnitz, GERMANY.

The molecular dynamics of confined (low molar and polymeric) systems is determined by the counterbalance between surface- and confinement-effects: Due to interactions with the (inner) surfaces (e.g. the formation of H-bonds, grafting, physisorption) the molecular dynamics is slowed down, resulting in an increase in the glass transition temperature of the system. In contrast the confinement may induce an increase in "free volume" thus making the molecular dynamics faster than in the bulk system. This causes a decrease in the glasstransition temperature. This counterbalance will be exemplified in the talk by employing broadband dielectric spectroscopy ( $10^{-2} \text{ Hz} - 10^9 \text{ Hz}$ ) to study the molecular dynamics of low molecular weight systems (ethyleneglycol, salol, etc.) and polymers (polyethers) being contained in mesoporous systems (MCM-48, pore-diameter 3.2 - 3.5 nm; MCM-41, pore-diameter: 2.5 nm). Furthermore dielectric measurements on grafted hairy rod-molecules (polyglutamates) in layer thicknesses of  $29 \pm 2 \text{ nm}$  and  $38 \pm 2 \text{ nm}$  will be presented and discussed with respect to the bulk system.

#### References:

1. A. Huwe, F. Kremer, P. Behrens and W. Schwieger Phys. Rev. Lett. Vol. 82, 11, p.2338-2341 (1999)

2. F. Kremer, A. Huwe, M. Arndt, P. Behrens and W. Schwieger J. Phys. Condens Matter 11, A175-A188 (1999)
3. F. Rittig, A. Huwe, G. Fleischer, J. Kärger and F. Kremer Phys. Chem. Chem. Phys. 1, 519-523 (1999)
4. M. Arndt, R. Stannarius, H. Groothues, E. Hempel and F. Kremer Phys. Rev. Lett. 79, 2077-2080 (1997)
5. L. Hartmann, Th. Kratzmüller, H.G. Braun and F. Kremer in press Chem. and Phys. Macro Rapid Commun. (2000)

#### 11:45 AM T8.8

ROCK WETTING CONDITION INFERRED FROM DIELECTRIC RESPONSE. Yani Carolina Araujo, Mariela Araujo, Herman Guzman, Reservoir Department, PDVSA Intevep, Caracas, VENEZUELA.

Wettability is a manifestation of rock-fluid interactions associated with fluid distribution in porous media. It can modify the petrophysical properties of reservoir rocks. Conventional wettability evaluation is performed by a sequence of spontaneous and forced displacements of different fluids into a porous sample, a method which is costly and time consuming. A new attractive approach is to estimate this quantity from dielectric measurements, since they can be done rapidly and economically. The dielectric frequency response of several rock samples of known wettability condition was studied in the range from 10 Hz to 100 MHz. Samples were saturated with brine and oil. The results confirm the strong influence of wetting condition. Water wet samples have significantly higher values of  $\epsilon'$  and  $\epsilon''$  (real and imaginary parts of generalized complex permittivity) than oil wet samples. In particular, the high frequency behavior of  $\epsilon''$  is most affected. Different regimes are identified as a function of frequency. They correspond to zones where different polarization effects are manifested. We quantify this effect and find a correlation with the modified Amott wettability index. Based on these findings we propose an experimental protocol for the indirect measurement of wettability at laboratory scale.

#### SESSION T9:

Chair: Virginie Pasquier  
Thursday Afternoon, November 30, 2000  
Room 313 (Hynes)

#### 1:30 PM \*T9.1

SPREADING OF ULTRATHIN LIQUID FILMS ON SOLID SURFACES. Gleb Oshanin, Michel Moreau, LPTL, University of Paris 6, Paris, FRANCE; Anne-Marie Cazabat, LPMC, College de France, Paris, FRANCE.

We develop a microscopic dynamical description of ultrathin molecular films spreading on solid surfaces. In terms of our approach, we determine analytically spreading rates, density profiles in spreading films and estimate the critical temperatures of the wetting/dewetting and liquid/surface gas transitions. Our analytical predictions are confirmed by available experimental data.

#### 2:00 PM \*T9.2

COULOMB LATTICE-GAS MODELS OF ADHESION: STATICS AND DYNAMICS. Yitzhak Shnidman, Polytechnic University, Dept of Chemical Engineering and Chemistry, Brooklyn, NY.

Adhesion between elastic bodies is mapped to a lattice-gas model with long-range Coulomb interactions. Minimization of its mean-field free energy with respect to the charge density relates equilibrium deformation and stress profiles at the surfaces of the adhering bodies to the interaction between the surfaces and to elastic constants. In practice, adhesion typically proceeds under external stresses driving such systems out of thermodynamic equilibrium. Resulting interfacial deformations and flows strive to relax towards equilibrium as dissipative processes with characteristic rates. Equilibrium models based on a minimization of a free energy then become inadequate. It will be shown how dynamic lattice-gas models, based on a Markov-chain description of dissipative processes, and on appropriate conservation laws, can be derived to model nonequilibrium dynamic effects in adhesion. Such models provide time evolution equations for interfacial deformations and stresses, and relate them to molecular interaction parameters and to schedules of separation and of loading/unloading forces. Results will be compared to experiments, and to other models in the literature.

#### 2:30 PM T9.3

RELAXATION METHOD SIMULATIONS OF CONFINED POLYMER DISPERSED LIQUID CRYSTALS IN AN EXTERNAL FIELD. J.J. Castro, R.M. Valladares, A. Calles, Faculty of Sciences, National Univ of Mexico, MEXICO.

Polymer dispersed liquid crystals (PDLC) are materials formed by

nematic liquid crystals droplets with radii of a few hundred Å embedded in a polymer matrix. We discuss the use of relaxation methods for the study of the response of the director of a PDLC under the switching of an external electric field. We simulate the confining system by considering different boundary conditions at the droplet surface.

#### 3:15 PM T9.4

EFFECTS OF SOLVENT TEMPERATURE ON THE DYNAMIC BEHAVIOR OF POLYMER BRUSHES. Aaron Forster, S.M. Kilbey II, Clemson University, Department of Chemical Engineering, Clemson, SC.

The dynamic behavior of polystyrene-polyvinylpyridine (PS-PVP) polymer brushes in toluene and cyclohexane was investigated using the surface forces apparatus (SFA). Preferential adsorption of the PVP block tethers the PS brushes to atomically smooth mica surfaces. Structural and frictional forces between opposing brush layers were measured as a function of solvent temperature and degree of compression. Experiments in cyclohexane were carried out at temperatures of 32, 40, and 50°C. Typical brush behavior was observed in the structural force measurements - the forces of interaction were monotonically repulsive. The onset of repulsion between the brush layers was measured at smaller gap distances in cyclohexane - (at all temperatures examined) - than in toluene. Over the temperature range studied, the surface separation distance at which repulsive forces are observed does not appear to be dependant on solvent temperature, indicating that brush height is not a strong function of temperature. The dynamic behavior, however, appears to be strongly influenced by temperature. For brushes in cyclohexane, as the temperature was increased from 32°C, the shear behavior tended toward that observed in toluene. This change in shear response of brushes as a function of temperature will be the main focus of our presentation.

#### 3:30 PM T9.5

MULTISCALE DYNAMICS IN COMPLEX IONIC MEDIA. Pierre Turq, Marie Jardat, Anne-Laure Rollet and Jean-Francois Dufreche, Université Pierre et Marie Curie, Paris, FRANCE.

Transport coefficients in charged media exhibit strong variations, according to the conditions of displacement of the particles. Electrical transport, characterized by the simultaneous displacement of positive and negative particles in opposite directions obeys Ohm's law, but its variation with concentration (non-ideality), depends on several types of interactions, whose time of establishment varies from picosecond to nanosecond. Several diffusion processes can occur: mutual diffusion, where ions move simultaneously in the same direction, keeping local electroneutrality, and self-diffusion where individual ionic particles move separately. The variation of diffusion coefficients with concentration depends on non-ideality factors analogous to those occurring in conductance, and their experimental evidence is facilitated by the availability of experimental techniques owing different characteristic times of observation. This phenomenon is particularly noticeable for self-diffusion coefficients, where the dynamical processes can be observed from the picosecond range (neutron quasi-elastic scattering), to millisecond (NMR) and to hour scale (radioactive tracers). The results are especially enhanced for porous charged media like ion exchanging membranes (nafions). Those results, as well in solution as in solid systems, are explained in the framework of continuous solvent model theories (brownian dynamical and analytical theories). The consistency of the non-ideality models and parameters for the different transport and equilibrium coefficients is examined carefully.

#### 3:45 PM T9.6

INFLUENCE OF WETTING PROPERTIES ON DIFFUSION IN A CONFINED FLUID. Jean-Louis Barrat, Lydéric Bocquet, Département de physique des Matériaux, Université de Lyon, Villeurbanne Cedex, FRANCE.

We show, using a hydrodynamic analysis and molecular dynamics simulations, how the wetting properties of a fluid/solid interface can indirectly influence the diffusion properties of fluid confined between two solid walls. This influence is related to the variability of the hydrodynamic boundary conditions at the interface, which correlates to the wetting properties. As an example, we study the case of water confined by two silanized surfaces.

#### 4:00 PM T9.7

INFLUENCE OF ALIGNMENT OF CRYSTALLINE CONFINING SURFACES ON STATIC FORCES AND SHEAR IN A NEMATIC LIQUID CRYSTAL. Marina Ruths, Steve Granick, Department of MS&E, University of Illinois, Urbana-Champaign, Urbana, IL.

The static force-distance relations and linear and nonlinear viscoelastic responses to oscillatory shear were studied of

4'-*n*-pentyl-4-cyanobiphenyl (5CB) confined between two muscovite mica surfaces at 25°C. The orientation of the crystallographic axes of the mica sheets was varied from close to perfect alignment to a twist angle of  $\theta > 80^\circ$ , and the sliding direction was kept parallel to the  $\gamma$  optical axis of one mica sheet. The effective shear moduli and limiting shear stress decreased with increasing film thickness and misalignment. In contrast to the known friction behavior of muscovite mica in the absence of an intervening fluid layer, no local extrema were observed at  $\theta = 30^\circ$  and  $60^\circ$ , indicating that the shear response resulted from the structure of the film of anisotropic molecules and not directly from the surface crystal lattice.

#### 4:15 PM \*T9.8

THERMOCAPILLARY FLOW ON PATTERNED SURFACES: A DESIGN CONCEPT FOR MICROFLUIDIC DEVICE. S.M. Troian, Dept. of Chemical Engineering, Princeton University, Princeton, NJ.

The miniaturization and integration of multiple functionality for chemical analysis and synthesis into a handheld device requires efficient methods for transporting ultrasmall volumes of liquid through networked arrays. The majority of devices in development combine micromechanical and electrokinetic techniques for controlling flow in enclosed microchannels. We recently introduced a non-electronic means of flow control that could eventually lead to the construction of a chemical reactor on the surface of an integrated circuit. The design concept relies on thermocapillary transport of liquid streams or droplets on a surface of mixed wettability produced by micropatterning a self-assembled monolayer. The chemical patterning confines the flowing liquid to selected pathways bearing a streamwise thermal gradient. A distinct advantage of this approach is that micropatterned temperature fields can eventually be used in differential mode to route liquid along selected pathways and in absolute mode to induce chemical reactions at electronically addressable sites.

The development and design of such an integrated microfluidic chip requires a fundamental understanding of thermocapillary flow on homogeneous and chemically micropatterned surfaces. We review modeling and experimental efforts describing the stability of thermocapillary driven flow on homogeneous surfaces and discuss extensions to chemically micropatterned ones. For microfluidic applications, we show that polar liquids can be routed on glass or silicon along surface pathways defined by hydrophilic lanes on a hydrophobic background. We investigate the speed of the moving liquid front and surface profile shape as a function of the lane width, the applied thermal gradient and the liquid material properties. A simple force balance applied to the moving front provides an estimate of the narrowest liquid stream transportable by this technique.