Programme Schedule

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Abstracts

IT–1

SOFT-EHL – THE TRIBOLOGY OF TYRES AND TONGUES

Connor Myant, Jason Stokes and Hugh Spikes
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There is growing interest in isoviscous-elastic or “soft-elastohydrodynamic” lubrication (soft-EHL). This normally occurs in lubricated, non-conforming contacts when one or both of the bodies is highly elastic, e.g. an elastomer or human tissue. This regime of lubrication is found in engineering systems such as lubricated seals, windscreen wipers and between tyres and wet roads. It is also prevalent in many biological systems, such as natural and replacement human joints, the tongue-palate contact during oral processing and in human skin and hair contacts treated with personal care products. Surprisingly thick hydrodynamic lubricant films can be formed in soft-EHL contacts, even by low viscosity lubricants such as aqueous solutions and this has practical relevance in both engineering and biological applications. This talk first describes work to measure rolling and sliding friction of a variety of fluids, ranging from simple Newtonian liquids to multiphase fluids, in soft-EHL contacts. It then presents a new technique for measuring and mapping film thickness in soft lubricated contact. The combination of friction and film thickness measurements forms a powerful tool for understanding the behaviour of lubricants at high shear rates and in thin film contact conditions.

IT–2

APPLICATIONS OF SURFACE ANALYSIS METHODS TO PROBLEMS IN TRIBOLOGY

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Surface analysis and the methods of surface science have been applied to a wide variety of problems in tribology over the past few decades. The contributions of surface science are two-fold. In many cases surface science has been used in an analytical mode to determine the composition, structure, and others relevant physical characteristics of tribological surfaces and materials. In its second mode of application, surface science has been used to prepare pristine and highly characterized materials surfaces for tribological studies aimed at isolating specific structure-function relationships relevant to tribology. The presentation will focus on the latter application of surface science to tribology.

Three surface science methods will be reviewed briefly in a short tutorial for those unfamiliar with their use: x-ray photoemission spectroscopy, low energy ion scattering spectroscopy, and temperature programmed desorption spectroscopy. These are used to determine the surface composition of materials, the chemical state of materials surfaces and to measure the adsorption energies of molecules on various surfaces.

Two applications of surface science methods will be described. The first will be the use of surface science methods to study and understand the properties of surfaces used in the magnetic data storage industry. The surfaces of hard disks are coated with thin carbon films (~3 nm) lubricated with even thinner (1 nm) films of fluorinated ether lubricants. Surface science methods have been used to study the properties of the carbon films used to protect hard disk surfaces and to understand the nature of the interactions of fluorinated lubricants with these carbon films. The second phenomenon that will be illustrated is that of surface segregation in alloys and multi component materials. Segregation is the phenomenon which leads to surface compositions of alloys being significantly different from those of the bulk. This is a generic property of multicomponent materials that is relevant to many technologies including tribology. The use of XPS and LEIS to study surface segregation in alloys will be illustrated. The presentation will conclude with a description of high throughput methods being applied to the study of surface segregation.

IT–3

SUPERLUBRICANTS FOR HARD STEEL CONTACTS

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We present here anomalous low friction in the superlubricity regime (friction coefficient below 0.01) obtained with highly polished steel on steel hard contacts lubricated by polyhydric alcohols (particularly glycerol) and some carbohydrates $C_x(H_20)y$ under severe mixed and boundary regimes. We investigated the effects of contact pressure, sliding speed, test duration and temperature on friction and electrical contact resistance. The mechanism of superlow friction is thought to have two (non-exclusive) origins: first a contribution of an ultrathin EHL film of glycerol molecules providing easy shear under high pressure; second a tribochemical decomposition of glycerol molecules inside the contact, generating organic acids or aldehyds, alkenes, gases (CO) and water in the ineterface film. The effect of deuterated glycerol on lowering friction is also shown. This new mechanism (called H-bond Network model) is completely different from the well-accepted "Monolayer" model operating with polar molecules containing long aliphatic chains. The possibility of a supercritical water lubrication mechanism is discussed in the light of Molecular Dynamics results.

Moreover, we show outstanding superlubricity of steel surfaces directly lubricated by a solution of myo-inositol (also called vitamin Bh) in glycerol at ambient temperature (25°C). Under boundary lubrication at high contact pressure, friction of steel is below 0.01 in the absence of any long chain polar molecules. Mechanism is still unknown but could be associated with friction-induced dissociation of inositol and H-bond interactions network of water-like species between OH-terminated steel surface.

CT–1

SQUEEZE OUT OF ORDERED AND DISORDERED MOLECULAR LAYERS

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* National University of Singapore, Singapore. # presently Leibniz Institute for New Materials (INM), Saarbrücken, Germany.

We discuss the use of AFM in liquid to both image molecules and measure the oscillatory solvation forces acting between the AFM tip and a HOPG graphite surface in linear and branched alkanes (hexadecane, squalane and heptamethylnonane or HMN). We use conduction AFM (C-AFM) to explore the squeeze out mechanics of these systems i.e. we simultaneously measure the surface force and the electrical conduction between tip and sample. This allows the relative tip-sample contact area to be found and to observe subtle changes within the contact zone which cannot be observed by monitoring the force alone.

The main result is that solvation layering occurs for all liquids but marked differences in the squeeze out mechanics are observed depending on whether the confined liquid molecules form ordered or disordered monolayers on the HOPG surface. The squalane monolayer at 25$^{\mathrm{o}}$C is an ordered solid (as verified by direct imaging) and the squeeze out is a step-like event and resembles that of other, more well known solid monolayers, such as hexadecane. Continuum elastic models appear well suited to describing the current-force data of ordered, solid-like material such as squalane and hexadecane. In contrast HMN is in a disordered state at 25$^{\mathrm{o}}$C and the force curves are qualitatively very different. The tip-surface contact cannot be modelled as a simple elastic asperity, even in solid-solid contact! We hypothesize that liquid-like HMN remains trapped in the contact zone even under very high pressure.

Our interpretations are supported by measurements at; different temperatures, where we observe a crossover from ordered to disordered monolayers as the temperature increases, with a corresponding crossover from solid-like to liquid-like squeeze out behaviour. Different tip-surface approach speeds, where we observe that at slow speed confined material has time to "move out" of the contact zone and a true solid-solid contact can be formed.

If time permits, we will also discuss some new measurement approaches for friction based on using microfabricated structures and specialized AFM tips.

CT–2

HIGH RESOLUTION DYNAMIC LATERAL FORCE MICROSCOPY OF SOLID/ LIQUID INTERFACES

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How is the behavior of liquid molecules near solid surfaces? The nature of structures and dynamics at solid/liquid interfaces would be of fundamental interest for many scientists, biologists, chemists and physicists. In this forum, we will focus on the structures of water molecules adsorbed on solid surfaces immersed in water. Figure 1 shows an atomically resolved image of a mica/water interface at room temperature obtained by dynamic lateral force microscopy. Cross sectional analysis of the image at a step (Fig. 2a) and a single protrusion (Fig. 2b) suggest that the adsorbed water molecules are structured and layered like ice Ih. To achieve the spacial resolution of atomic scale, the tip amplitude for lateral direction to the surfaces was reduced down to 1.3 Angstrom. The small tip motion for lateral direction allowed us to observe the layered structures of water molecules at the mica/water interface without disturbing the structures. We used the first torsional mode of a silicon cantilever with the frequency of 1.15 MHz, which was photothermally excited, and was detected using laser Doppler velocimetry. The imaging was operated using phase-modulation technique, because the clean stimulant signal supplied from a signal generator stabilized the cantilever vibration in water.

Fig. 1

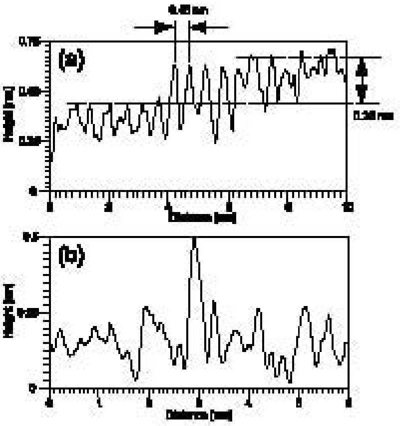

Fig. 2

CT–3

MECHANICAL RESPONSE AND FINE STRUCTURE OF A CONFINED MODEL FLUID

Tobias E. Balmer[1], Nicholas D. Spencer1 and Manfred Heuberger[1,2]
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[2] Empa, Materials Science & Technology, St. Gallen, Switzerland

Certain liquids exhibit a significant deviation from bulk fluid behavior when confined to very thin films between atomically smooth surfaces. The surface forces apparatus (SFA) is an established tool to study the physical properties of such confined fluid films. SFA experiments also provide important input for theoretical work describing this new physics. One of the first model systems studied was the simple liquid octamethylcyclotetrasiloxane (OMCTS). This non-polar liquid is known to exhibit oscillatory surface forces when confined between molecularly smooth sheets of muscovite mica, which is due to the diffuse layering of the quasi-spherical molecules parallel to the solid interface. The amplitude and (exponential) decay of force maxima seems to vary significantly between experiments, indicating that small variations must play an important role. Recent experimental studies also underline the dimensional anisotropy of molecularly layered fluids, i.e. in-plane fluid-like behavior opposing out-of-plane solid-like behavior. The relationship between molecular structure and macroscopic force is not yet fully established.

Using the extended surface force apparatus (eSFA) we revisited the oscillatory force profile of OMCTS and produced unprecedented data quality. We have scrutinized the mechanical response, i.e. uni-axial compression, of the layered liquid. We discuss the necessary data correction due to the compression of the mica surfaces to measured film thickness - an effect that becomes relevant already for relatively low (normalized) forces of 1-2 mN/m. For the first time we present a corrected force curve that allows discerning layering transitions from the one-dimensional solid compressibility of the model fluid OMCTS. In a second step we have analyzed in detail the interlayer distance provided by the oscillatory force data. The results reveal new insight pertaining to the molecular arrangement of the layered liquid. Here, an important finding is that the OMCTS molecules form interpenetrating layers, imposing an in-plane correlated fluid, whilst the layer interdiffusion rates are largely suppressed in the solid-like out-of-plane dimension.

The mechanical behavior of the confined fluid changes dramatically if only trace amounts of water are present in the system. This is due to the formation of an adsorbed water layer at the mica-OMCTS interface. In combination with a novel method, called the transmission interferometric adsorption sensor (TInAS) [1], the eSFA is capable of measuring the thickness of such fluid-fluid-solid adsorbate layer as a function of the relative humidity and correlate it with in-situ force measurements. Finally, we discuss the underlying molecular structure of layering OMCTS in the presence of water.

[1] Heuberger, M. and T.E. Balmer, J. Phys. D, 2007. 40: p. 7245-7254.

CT–4

WATER STRUCTURE AND FORCES BETWEEN HYDROPHILIC SURFACES

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There is considerable interest in developing a molecular understanding of the structure and state of water confined between hydrophilic surfaces. Using grand ensemble simulations with the SPC/E (simple point charge/ extended) model for water we have analyzed layering and hydrogen bonding characteristics of confined water as a function of the separation between two mica surfaces. At large surface separations, density distributions of water compare well with the X-ray reflectivity studies on a single mica surfaces. At small surface separations of 0.4 - 0.5 nm, water is seen to form a well ordered single sheet like structure in the nanopore. Examining the in- lane pair correlation function of the oxygen atoms in the plane of the potassium ions reveals the formation of an ordered structure. This situation is observed for surface separations ranging from 1.0-4.0 nm. This system does not have solvation force oscillations as observed for confined nonpolar fluids. We also investigate and contrast the salvation force characteristics for water confined between hydroxylated silica surfaces. Although both surfaces are hydrophilic, oscillatory salvation forces are observed only in the water/silica system. Analysis of the structural variations that give rise to the solvation force differences between these two systems is discussed.

CT–5

OBSERVING CONTACT MECHANICS IN TRANSMISSION ELECTRON MICROSCOPE

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Transmission Electron Microscope (TEM) has the ability to look through the material at very high magnifications. It enables direct visualisation at nanoscale of not only the contacting surfaces but also the subsurface deformation resulting from the contact interaction. Dynamic real time observations will be the first step in deciphering the mechanisms of friction and wear. With the help of a specimen holder developed two surfaces can be brought in contact and moved relative to each other while observing the contacting interfaces at high magnifications in JEOL 2000FX microscope.

The piezoelectric translator based construction has resulted in a high stiffness displacement controlled instrument that can measure the instabilities resulting from the attractive forces as the surfaces are moved closer to each other. The material pairs that can be studied are limited only by the TEM specimen preparation techniques. Different types of experiments have been designed to study the contact mechanics at the nanoscale bringing out the capabilities of the instrument. These experiments have been used in studying Single asperity indentation, Mechanics of the Atomic Force Microscope tips while scanning and the delamination failure of the tribolayer.

CT–6

DIRECT OBSERVATION OF ONSET OF PLASTICITY AND MECHANICAL RESPONSE OF MATERIALS AT NANOSCALE CONTACT INSIDE A TEM

Dr. S.A. Syed Asif
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Studying the mechanical response such as nucleation and multiplication of dislocation at nanoscale is central to our fundamental understanding of deformation behavior of materials. An important descriptor of the mechanical response of a material is its theoretical or ideal strength. This is the strength which an ideal, defect-free crystal can sustain. In bulk materials, because of the high concentration of intrinsic defects, the yield strength is very much reduced and it is generally believed to be scale independent. When element length approaches the nanometer scale, it is no longer clear whether traditional mechanical properties like yield strength and hardness are valid concepts, or if such properties of larger structures of the same material can be used to describe a nanostructure. In recent years, depth sensing nanoindentation emerged as a standalone technique that enabled mechanical response and property measurements such as hardness and elastic modulus at depths as shallow as a few nanometers. However, at shallow depths, the load-displacement curves often exhibited unusual features such as pop-in/pop-out load-displacement discontinuities which required additional characterization to uncover their source. Coupling depth sensing nanoindentation to transmission electron microscopy (TEM) in an in-situ, quantitative manner represents an attractive way of time correlating an unusual feature of a force-displacement curve to the corresponding change in the microstructure of the sample being indented. This talk will demonstrate this capability from results on the in situ TEM nanoindentation and compression of nanograin Al thin films, single-crystal silicon, CdS nanoparticles and single crystal Ni nano pillars. The preliminary results will be reported and the physical insight regarding dislocation nucleation and multiplication derived from these results will be discussed. Based on the experimental evidence a new view of the onset of plasticity in materials will be presented.

CT–7

THE INFLUENCE OF NANOPARTICLES ON THE TRIBOLOGICAL BEHAVIOR OF PEEK-BASED TRIBOMATERIALS

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Nanoparticle reinforced polymers attract more and more attention due to their unique properties resulting from the nano-scale structures. To meet the requirements for light weight and high wear resistance, formulations of polymer based nanocomposites become an important issue. In the first part of this work, the tribological mechanisms of pure PEEK and short carbon fiber (SCF)/PTFE/graphite (micro-sized) reinforced PEEK are briefly reviewed. The second part of this work reports our most recent results dealing with the roles of nano-SiO_2 particles (13 nm) on the sliding tribological behaviors of PEEK and SCF/PTFE/graphite reinforced PEEK.

The results of tensile tests indicate that when low-loading nano-SiO_2 (from 0.5 vol.% to 4 vol.%) is incorporated into PEEK the matrix stiffness is remarkably increased. The wear resistance of PEEK is significantly improved by incorporating nano-SiO_2 and at a rather low nano-SiO_2 loading, i.e. 1 vol.%, the composite presents the optimum wear resistance. The reduced perpendicular deformation of the PEEK matrix and the reduced tangential plastic flow of the surface layer involved in the friction process are supposed to be important for the modification in the tribological behavior after incorporating nano-SiO_2.

The incorporation of 1 vol.% nano-SiO_2 particles into SCF/PTFE/graphite (10 wt.% for each) reinforced PEEK remarkably decreases the friction coefficient of the traditional fillers reinforced composite. With respect to the wear rate, however, the roles of the nanoparticles show a strong dependence on friction conditions. Under pressures higher than 2 MPa, the nanoparticles significantly decrease the wear rate. This effect is more pronounced under high pressures and especially at high sliding velocities. For example, the low-loading nanoparticles result in a wear reduction of 73.5% under 5 MPa at 2 m/s. The characterizations of worn surfaces suggest that the improvement in fatigue resistance of SCF/PEEK interface by incorporating nanoparticles is the major reason for the reduction in the wear rate.

CT–8

MOLECULAR ENGINEERING OF HIGH PERFORMANCE LUBRICANT BASE OIL (GROUP III & IV) BY NANOCATALYST AS STUDIED BY NMR SPECTROSCOPIC TECHNIQUES.

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The understanding of the relationship between the hydrocarbon molecular structure and physicochemical properties help in the formulation of a desired lubricant system. The Group III-IV Base oils produced by catalytic dewaxing and wax hydro isomerisation (Isocracking) technology are composed of Specific Isoparaffinic molecular structures demonstrating excellent Visco-Temperature-pressure characteristics (high VI, low Pour Point, small EHD film thickness etc.). The role of catalyst is very important in cracking and producing a desired composition of lubricant base oil

The present studies discuss role of Nanocatalyst in the molecular engineering of a lubricant molecule which constitutes the High Performance Group-III&IV Base oils. The structural features of Nanocatalysts, which are responsible for the engineering of a desired molecules imparting the superior physico-chemical properties to the Group III & IV Base oil, have been characterized by NMR spectroscopic techniques. A detailed description of Molecular Structure of hydrocarbons present in the high performance group111 & IV base oils as derived from the NMR spectral studies have been correlated with the Visco-Temperature-pressure characteristics. The main focus is on the similarity in the Molecular isoparaffinic structures of Group III & IV base oils and their relationship with the Physico-chemical properties (VI, PPt, Oxidation stability, EHD film etc.). The characteristics of a future ideal high-performance hydrocarbon molecule with the desired properties for reducing friction in the automotive engine oil applications as engineered by Nanocatalyst have been proposed.

IT–4

PEELING SINGLE STRANDED DNA FROM GRAPHITE

Anand Jagota
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We measured the force required to peel single-stranded DNA molecules from ingle-crystal graphite using chemical force microscopy. Force traces during retraction of a tip chemically modified with oligonucleotides displayed characteristic plateaus with abrupt force jumps, which we interpreted as a steady state peeling process punctuated by complete detachment of one or more molecules. We were able to differentiate between bases in pyrimidine homopolymers – peeling forces were 85.3±4.7 pN for polythymine and 60.8±5.5 pN for polycytosine, substantially independent of salt concentration and the rate of detachment. We developed a model for peeling a freely jointed chain from the graphite surface and estimated the average binding energy per monomer to be 11.5±0.6 k_BT and 8.3±0.7 k_BT in the cases of thymine and cytosine nucleotides. The equilibrium free-energy profile simulated using molecular dynamics had a potential well of 18.9 k_BT for thymidine, showing that non-electrostatic interactions dominate the binding. The discrepancy between the experiment and theory indicates that not all bases are adsorbed on the surface or that there is a population of conformations in which they adsorb. Force spectroscopy using oligonucleotides covalently linked to AFM tips provides a flexible and unambiguous means to quantify the strength of interactions between DNA and a number of substrates, potentially including nanomaterials such as carbon nanotubes.

IT–5

STICKY FINGERS HELP! - SINGLE MOLECULE CUT AND PASTE

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Molecule by molecule assembly of functional units promises a wide range of new applications in different fields of nanotechnology. In this lecture a new method for the bottom-up assembly of biomolecular structures is introduced, which combines the precision of the atomic force microscope with the selectivity of DNA hybridization. Functional units coupled to DNA oligomers were picked up from a depot using a complementary DNA strand bound to an AFM tip. These units were transferred to and deposited on a target area. Each of these cut and paste events were characterized by single molecule force spectroscopy. Using this technique basic geometrical structures were assembled from units with different functions. The precision of the assembly and the accuracy of the quantification by force spectroscopy were confirmed by single molecule fluorescence microscopy using TIRF excitation. We demonstrated the reproducibility and robustness of this new technique through the transport and deposition of more than 5000 units without significant loss in transfer efficiency. This technology was furthermore used to write ligand pattern for the assisted self assembly of nanoparticles.

Kufer S., Puchner E. M.,Gumpp H., Liedel T., and Gaub H. E. Single molecule cut and paste surface assembly. Science (2008), Vol 319, p 594

IT–6

MECHANOBIOLOGY OF GENOME ASSEMBLY & REGULATION

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Genomic DNA, which is almost a meter long, is remarkably efficiently packaged into the cell nucleus, hardly a few microns across, using histones and other nuclear proteins. Recent evidence suggests that the extent and form of such packaging (chromatin) within living cells is central to its gene expression pattern and hence function. Further, gene expression patterns in cultured cells or cells within an organism, are responsive to nanoscale mechanical forces experienced at the cell membrane that are transduced into biochemical signals to alter genome function. However the physical basis behind the creation and maintenance of genome assembly & its subsequent modulation in the context of its function are unclear. Progress in high resolution live-cell imaging combined with biomechanics and functional genomics developed in many laboratories including ours have provided a new paradigm in understanding genome regulation. Using a multi-disciplinary approach, our laboratory studies the impact of cellular architecture in governing genome assembly and its regulation. For this we use mammalian cell lines, stem-cells undergoing differentiation and developing Drosophila embryos as model systems. We address in living cells and embryos, the spatio-temporal variation in the compaction of the genome assembly during differentiation and development and correlate these changes with cellular transcription control and memory. We have obtained insights into the mechanical coupling of cellular architecture on genome organization by controlled physical manipulation of the latter. Such controlled physical modulation of genome architecture could pave the way to artificially engineering transcription programs in diverse developmental contexts for cell/tissue engineering applications. In this talk I will discuss some of our recent experiments outlining our insights in these directions and the implications of the physical coupling of genome organization to cellular architecture.

Selected publications (2006-2008):

- Probing the dynamic organization of transcription compartments and gene loci within the nucleus of living cells Deepak Kumar Sinha, Bidisha Banerjee, Shovamayee Maharana, & G.V.Shivashankar (Biophysical Journal – in press08: accompanied with a new & notable article)
- Dynamics of chromatin decondensation reveals the structural integrity of a mechanically prestressed cell nucleus Aprotim Mazumder, T.Roopa, Aakash Basu, L.Mahadevan & G.V.Shivashankar (Biophysical Journal – in press08)
- Gold-nanoparticle-assisted laser ablation of chromatin assembly reveals unusual aspects of nuclear architecture within living cells Aprotim Mazumder & G.V.Shivashankar Biophysical Journal (2007) 93, 2209-2216
- Direct measurement of chromatin fluidity using optical trap modulation force spectroscopy, T.Roopa & G.V.Shivashankar Biophysical Journal – (2006) 91, 4632-4637
- Core and linker histones diffuse via distinct mechanisms within living cells Dipanjan Bhattacharya, Aprotim Mazumder, M.Anne & G.V.Shivashankar Biophysical Journal (2006), 91, 2326-2336
- Chromatin assembly exhibits spatio-temporal heterogeneity within the cell nucleus Bidisha Banerjee, Dipanjan Bhattacharya & G.V.Shivashankar, Biophysical Journal (2006), 91, 2297-2303 (Cover page)

IT–8

BOTTOMUP DESIGN OF MECHANICALLY STRONG CARBON NANOTUBE MEMBRANES

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Directed self assembly of nano fibrous materials is a “bottomup” approach which has potential to manufacture nanocomposite materials with enhanced properties. The approach is advantageous as the selfassembly process is spontaneous, requires no human intervention at the nanoscale and can be controlled via convenient macroscopic control parameters.

However, despite great progress experimental investigation of the nanoscale structure of these materials remains challenging and expensive. Computer simulations on the other hand are well suited for the small length scales relevant to these materials and offer the opportunity to synthesize”, investigate and test the nanoscale structures in the same simulation framework. Here we study self assembly of surfactant molecules on crossing carbon nanotubes, the primary building block of a carbon nanotube membrane, using the dissipative particle dynamics method. At the right thermodynamic conditions the molecules aggregate at the crossings only and join them together. In the same simulation we are able to investigate the mechanical properties of the joints to get a first glimpse at the strength of the nanotube membrane.

IT–9

ELASTICITY OF dsDNA, JX AND PX DNA NANOSTRUCTURES

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DNA and its crossover motifs are integral components for designing DNA based nanostructure and nanomechanical devices. Knowledge of the mechanical strength of these structures under various conditions is very important for their use in these applications. We study the structural rigidity of dsDNA, paranemic crossover (PX) and its topo-isomer JX DNA nanostructures under the external force using fully atomistic molecular dynamics simulations. In the presence of mono-valent Na+ ions, we find that the stretch modulus (S) of PX and JX DNA structure is significantly higher (almost 30%) compared to that of normal B-DNA of the same sequence and length. The stretch modulus is also found to depend strongly on the rate of pulling due to the dynamical stiffening of the molecular bonds which increase with the rate of forcing. Similar trend for stretch modulus and its dependance on rate of force was found in the presence of di-valant Mg+2 ions also. We also give a molecular level picture of these DNA molecules under various stretching forces. This is the first direct determination of the mechanical strength of these DNA motifs which can be useful for design of suitable DNA structure with improved structural rigidity.

IT–10

SHORT RANGE INTERACTIONS BETWEEN PHOSPHOLIPID BILAYERS: DISECTING THE FORCES

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Short range interactions between soft interfaces are important for the understanding of biolubrication and biofriction. Here the grand canonical Monte Carlo technique is used to reveal the origin of the repulsive pressure operating between supported DLPC bilayers at short separations. By partitioning the interbilayer pressure into physically distinct components, it is shown that the short-range repulsion comes mainly from the direct electrostatic lipid-lipid interaction of the head groups in the opposing leaflets. By contrast, the electrostatic lipid-lipid interaction between DLPE bilayers is strongly attractive, and the short-range repulsion is associated with the hydration (water-lipid) interactions [A. Pertsin, D. Platonov, M. Grunze, Langmuir 23 (2007) 1388]. These findings explain why DLPC bilayers have a much larger interbilayer (fluid) separation at a given pressure, as compared to that for DLPE.

IT–11

FRICTION FORCE MICROSCOPY: CONTACT MECHANICS AND APPLICATIONS IN THE ANALYSIS OF POLYMERS, MONOLAYERS AND NANOSTRUCTURES

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Besides offering insights into origins of interfacial phenomena such as friction and lubrication, friction force microscopy (FFM) also provides a powerful tool for surface analysis because of the sensitivity that it exhibits to nanometre-scale variations in chemical composition and structure. For all these applications, an adequate understanding of the relationship between measured forces and surface molecular structure is required. The contact mechanics of the tip-sample interaction have been studied for a variety of model self-assembled monolayer (SAM) and polymer systems in different media. The nature of the medium influences not only the strength of interaction, but also the nature of the contact mechanics. For all systems, the relationship between the friction force and the load is linear in ethanol, in conformity with Amontons' Law, but in perfluorodecalin and hexadecane, the contact mechanics are consistent with the predictions of the Johnson-Kendall-Roberts model for strongly adhering systems (eg the interaction between carboxylic acid functionalised tips and surfaces) and with the predictions of the Derajuin-Muller-Toporov model where the tip and the sample are dissimilar (for example, an acid-methyl contact).

In ethanol, the linear friction-load relationship enables determination of a coefficient of friction that may be used to characterise a particular tip-sample combination. The coefficient of friction so-determined provides quantitative data on both molecular organisation and surface chemical structure. For films of polystyrene (PS) and poly(methylmethacrylate) (PMMA), the coefficient of friction was found to increase rapidly with polymer molecular weight up to a point corresponding, approximately, to the critical molecular weight for entanglement MC. Thereafter, the coefficient of friction changed little with molecular weight. It is suggested that below MC, the viscosity of the film increases with molecular weight, leading to an increased rate of energy dissipation. Above MC, the tip-sample interaction is rather different, with the tip catching and pulling loops of polymer between entanglements. For PMMA, measurements of the coefficient of friction provide a convenient means of monitoring the rate of unzipping during UV exposure.

Measurements of the coefficient of friction of self-assembled monolayer systems enable the determination of changes in surface composition. As an illustration, data are provided for the derivatization of hydroxyl terminated SAMs using trifluoroacetic anhydride (TFAA). Using X-ray photoelectron spectroscopy and contact angle measurement, it is possible to determine that the kinetics of the reaction fir the Langmuir isotherm. Measurements of the surface composition (the mole fraction of unreacted hydroxyl groups, for example) may be made by analysis of FFM data, and the resulting compositional data have been found to agree remarkably closely with data from XPS. Using a variety of related, but comparatively simple, approaches, it is possible to make measurements of the surface composition in structures with dimensions of only a few tens of nm fabricated using scanning near-field photolithography, emphasising the importance of FFM as an analytical tool for applications in nanoscience.

IT–12

MECHANICAL AND FRICTIONAL PROPERTIES OF NANO-STRUCTURED POLYMER THIN FILMS

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Experimental surface forces studies of different classes of solvated polymer- and nanoparticle- bearing surfaces were carried out using the surface forces apparatus and similar molecular techniques in order to elucidate the role of different parameters, such as molecular conformation, surface roughness and elasticity, solvent quality, ionic strength, in controlling friction and adhesion between surfaces.

To determine structure/property correlations, we irreversibly attached the polymer materials onto modified mica and silica surfaces with a controlled surface density. Controlling the grafting density of the polymer can be achieved by end-grafted polymers, resulting in one parameter by which control over polymer conformation and surface roughness is possible. Given the possibilities of irreversibly attaching polymers at surfaces, we examined systematically the effect of grafting density and environmental conditions on the surface forces and mechanical properties of different polymer-bearing surfaces. An example of nano-structured polymer surface is shown in Figure 1.

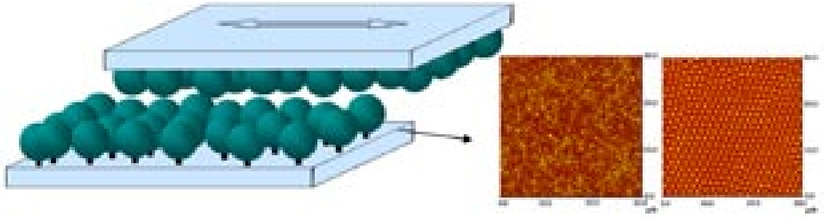

Figure 1. Schematic representation and surface imaging of monolayers of grafted hydrogel nanoparticles with two different surface densities and roughness.

CT–9

PROMOTING COLLABORATIVE RESEARCH IN EUROPE AND BEYOND: THE ESF AND EUROCORES PROGRAMMES

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The European Science Foundation (ESF) is an independent, non-governmental organization of 77 national research organizations from 30 countries.
Since its establishment in 1974, ESF has assembled a host of research organisations that span all disciplines of science in Europe, in order to create a common platform for cross-border and multidisciplinary cooperation.

The mission of ESF is to advance European research and supports basic research across all disciplines, through its activities and instruments, such as Research Networking Programmes, Exploratory Workshops and EUROCORES.

The EUROCORES are European Collaborative Research Programmes, provide national funding agencies with a framework to join forces to support transnational research across all fields of science. The main characteristics of EUROCORES programmes are the bottom-up approach (the scientists suggest the topic) and the funding which remain national while the coordination and networking is through the ESF.

FANAS (Friction and Adhesion in Nanomechanical Systems) is one of the 32 EUROCORES Programmes currently in the research phase. It was launched in June 2007 and will run until 2010. The aim of the EUROCORES programme FANAS is to get a better insight on the origins of friction and adhesion and to learn how to control them. The FANAS Programme comprises of 7 CRPs, with a research budget of over 7 million Euros, providing funding for 40 research groups in 14 countries.

In this talk the ESF, the EUROCORES Programmes and FANAS will be presented in detail.

CT–11

MECHANISMS OF ATOMIC FRICTION

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Force microscopy is a versatile instrument to investigate physical phenomena on surfaces. The first emphasis is on the study of friction on the nanometer-scale, also called nanotribology. It will be shown that atomic-scale stick-slip is relatively well understood, where the dependence on velocity and normal force is experimentally investigated and interpreted in terms of an extended Tomlinson model. It is essential to include thermal actuation to understand the observed phenomena. The transition from atomic-scale stick slip to continuous sliding will be described [1]. The detailed analysis yields the energy corrugation and the lateral contact stiffness as a function of load. Very low lateral contact stiffness values of the order a few N/m are found. In addition, experiments will be shown to determine the normal contact stiffness, simultaneously. Recently, it has been shown that atomic friction can be controlled with rather high accuracy by electrostatic actuation [2].

[1] A. Socoliuc, R. Bennewitz, E. Gnecco and E. Meyer, Transition from Stick-Slip to Continuous Sliding in Atomic Friction: Entering a New Regime of Ultra-low Friction, Phys. Rev. Lett. 92, 134301-1 (2004).

[2] A. Socoliuc, S. Maier, O. Pfeiffer,E. Gnecco, A. Baratoff, R. Bennewitz and E. Meyer, Atomic-Scale Control of Friction by Actuation of Nanometer-Sized Contacts" Science, 313, 207, July 14 (2006).

CT–12

MINIMALISTIC MODELS OF ATOMIC SCALE FRICTION.

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The Tomlinson model has proven powerful in describing the dynamics of friction and in reproducing many of the phenomena observed experimentally. Generalizations of the original, one-dimensional Tomlinson model, which included effects of two-dimensional structure of surfaces, lateral-normal coupling, and thermal fluctuations, marked new steps toward understanding and implementation of frictional phenomena. In particular they led to the introduction of frictional imaging of interfaces, mechanical control of friction and thermolubricity.

In this lecture I will discuss various generalizations of the Tomlinson model. I will focus on a new approach to describe the effect of coupling between translational and rotational motion of sliding surfaces on friction. The proposed model allows to explain experimental observations of finite 'lifetime' of a superlubric state which have been found measuring friction between a graphite flake attached to the tip of the frictional force microscope and an atomically flat graphite surface [1].

In addition temperature dependence of atomic scale friction will be discussed. Our recent simulations suggest a novel mechanism for nonmonotonous dependence of friction on temperature.

1. A. E. Filippov, M. Dienwiebel, J.W.M. Frenken, J. Klafter and M. Urbakh, Torque and Twist against Superlubricity, Phys. Rev. Lett. 100, 046102 (2008).

CT–14

NANOPARTICLE MANIPULATION BY ATOMIC FORCE MICROSCOPY TECHNIQUES

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Atomic force microscopy (AFM) has proven to be a powerful tool to investigate frictional forces of nanoscale contacts. Unfortunately, this technique reveals some drawbacks when applied to study chemical and structural properties of two rubbing surfaces. Questions concern the contact area dependence as well as the influence of the material on tribological properties. The contact area dependence of friction is crucial in bridging the gap between nanoscale and microscale friction, which eventually will allow to understand and control macroscopic friction. The right choice of materials, on the other hand, is expected to lead to new friction effects, like, e.g., superlubricity.

In this Collaborative Research Project AFM will be used to investigate nanoparticles with different sizes, shapes and functional groups on their surfaces, as well as substrates with different roughness, structure and chemical composition in different environments, from liquids to ultrahigh vacuum. The experimental studies are harmonized with theoretical investigations concerning the manipulation process itself, as well as the interfacial atomic processes during particle translation.

CT–15

ADSORPTION AND DEPLETION OF POLYMERS AT AN INTERFACE: AN EXPERIMENTAL STUDY

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Many additives are added to the base oil to improve the performance of the lubricant. Such additives include dispersants and viscosity improvers. The former keeps in suspension the impurities formed during operation of mechanical devices such as internal combustion engines. Viscosity improvers are used to reduce the extent of the decrease in viscosity as the temperature is raised or the increase in viscosity as the temperature is lowered, or both. Mixtures of conventional dispersants with polymeric viscosity improvers are often used but such combinations are costly. Therefore multifunctional additives that provide both viscosity improving properties and dispersant properties, known as Dispersant-Viscosity Modifiers, are generally prepared by functionalized a hydrocarbon polymer. The DVM efficiency is strongly controlled by the nature of their affinity with the base oil and their interactions with surfaces in case of confinement.

A molecular tribometre derived from a Surface Force Apparatus has been used to characterize the mechanical and tribological behaviour of two semi-dilute DVM solutions in a confined interface. At large distances, two regimes can occur:
(a) one polymer sticks to the wall and an adsorption layer is depicted,
(b) the other one is repelled by the wall and a depletion layer is built-up.

The structure of these layers results in a gradient of viscosity from the wall to the bulk which can be mechanically modelled.

The confinement at short distances governs the tribological behaviour of the polymer layer formed close to the surface.

CT–16

MICROSTRUCTURAL HETEROGENEITY IN ORGANIC MONOLAYERS

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Organic monolayers have been of immense interest due to their potential applications in lubrication technology. Chain length, backbone of molecules, and the interaction between the head group and the substrate impart considerable role in structural organization and stability of the monolayer. Here, lateral force microscopy is used to probe the morphological changes at the interface brought about when an octadecyltrichlorosilane (ODTS) monolayer self-assembled on a silicon surface, is slid against a Si_3N_4 tip in the 0-30 nN load range. High contact angle (θ_{water} =109º) and FTIR studies reveal the conformationally ordered structure of ODTS monolayer. However, AFM study shows a morphologically heterogeneous structure of monolayer; to be made up of tiles of characteristic friction forces and each tile is in a unique physical state. The variation of area fraction (in a scan area) of each tile is tracked as a function of normal load. It is observed that at low load, friction force is dominated by the crystalline tiles (low friction) and at high load area of amorphous tiles became dominant because of defect accumulations. The detail on structural organization of each tile as a function of normal load will be discussed during the presentation. The area averaged friction force at a load is obtained by summing the fractional forces of constituent friction tiles. The friction force obtained thus is found to vary linearly with normal load. The friction force of disordered monolayer, saturated with gauche defects, was found to be nearly steady with changing the load. This suggests that for a self- assembled monolayer the load governance of friction as implied by the Amonton's Law may be attributed to the physical changes that are brought about at the interface by changing the normal load.

CT–17

POLYMER SQUEEZE FLOWS AND MOLECULAR CONFINEMENT

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Nanometer-scale polymer squeeze flow is governs the dynamics of nanoimprinting and is important for boundary layer lubrication. Confinement affects the polymermechanics, causing deviations from normal property scaling. Low strain flow has been extensively studied, but there is rather less information available on high strains despite their key role in both imprint and tribology. Using a flat punch nanoidentation system, we have measured stress-strain behaviour during extrusion of monodisperse polystyrene molecules as molecularly thin films, at a range of temperatures. Standard polymer scaling is shown for thicknesses well above Rg. For very thin films, an overall stress reduction with strain appears regardless of molecular weight or processing conditions. In addition, when film thickness spatially confines the bulk macromolecule, a further reduction in stress appears at large strains, increasing proportionally as process conditions go from solid forging to liquid moulding. It is shown that squeeze flow is accelerated at small scales by an unexpected influence of film thickness scaling on large strain polymer forming. Some tribological consequences are also considered.

CT–18

NANO-SCALE SHAPE-MEMORY FUNCTION IN HIGHLY CROSS-LINKED POLYMERS

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Shape memory polymers can be deformed into a high strain state, store the deformation at low temperature and relax back to the undeformed state upon heating. This process has wide application as an actuation principle in restricted geometries in surgery, biomedical devices or micro systems. We investigate the effect in highly cross-linked polymeric thin films on the nanometer scale with the main focus for application on data storage in form of nanoscale polymer indentations.

Highly cross-linked polystyrene and a poly-aryletherketone (PAEK) derivative polymer were studied. The indents are written with precisely controlled force and temperature pulses using heated silicon tips. The duration of the pulses is in the range of 10 micro seconds. The indents consist of a circular depressed region in the centre, the pit or actual indent, surrounded by an elevated region, called the rim. Independent of the nature of the polymer, the original state of the surface can be recovered not only by annealing at elevated temperatures but also by utilizing the stress and temperature field emanating from neighbouring indents.

The stability of the deformed state of the polymers is measured as a function of annealing temperature and time. The annealing temperatures are always lower than the glass transition temperature of the polymer. The observed relaxation is shape preserving and follows a logarithmic time law. Moreover, indents of similar depth decay less fast if they are written at higher temperatures. All observation can be accurately modelled using a simple thermally activated barrier model where the barrier is lowered by the induced stress within the indents. The experimentally observed barrier heights of 1.5-2.5 eV for polystyrene and >6 eV for PAEK are in good agreement with yield activation energies found in literature of similar polymers. The model allows for extrapolation of the decay behaviour to lower temperatures and longer times. For the PAEK polymers a retention time of more than 10 years is extrapolated for temperatures below 85 deg C, which is sufficient for data storage applications.

Indents can also be forced to relax by exploiting a non-linear interference between closely spaced indents. The depth of a first written indent decreases as soon as the rim of the second indent overlaps with the trough of the first one. The erase activity can be expressed in terms of a universal function, independent of the tip opening angle and indentation temperature. Using this thermo-mechanical erase scheme, large indent fields can be erased whereby the original surface is recovered with sub nano-meter precision. Moreover, the process can be repeated more than 104 times without noticeable fatigue of the polymer. We argue that the shape memory effect is caused by metastable □-transitions, which are enabled by stress-assisted thermal activation.

CT–19

NANOTRIBOLOGY AND DIRECT FORCE MEASUREMENTS RELATED TO MOS2 AND WS2 NANOPARTICLES

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Layered materials such as MoS_2 and WS_2 (platelets of the 2H polytype) are used both as solid lubricants and as additives to improve the performance of mineral oils and greases under conditions of boundary lubrication. The low friction of these particles are due to the interplanar mechanical weakness, intrinsic to their crystal structure, that allows easy and low strength shearing. Hexagonal 2H-MoS_2 (Avg. particle size (APS) ~ 2µm and ~ 50nm) and 2H-WS_2 (APS ~ 600nm and ~ 50nm) nanoparticles have been assessed as additives for mineral oils under loading condition and we explore the tribological behavior of the particles; spin coated on steel substrate (dry) and dispersed in hexadecane for nanotribometry.

To explore the effect of size of the particles on friction, we study the nanotribological behavior of MoS_2 and WS_2 powders of two different particle sizes. The experimental results clearly show that friction increase with decreasing size of the 2H platelets. This observation is in agreement with the suggestion that dangling bonds mediate friction in metal dichalcogenides: as the average size of the platelets decreases, the total surface area and hence the number of dangling bonds on the reactive surface increases. This behavior is corroborated by the results of TGA and XRD of the respective particles.

Tribological nanoscale analysis using Atomic Force Microscopy in ambient, water and hexadecane medium were performed and the adhesion and lateral forces were measured between the AFM tip and the particle surfaces. The relationship among data from friction coefficient distribution, surface composition and particle size are compared and are presented. This data is used to provide a rationale for the tribological behavior observed in nanotribometry.

CT–20

FRICTION-DOMINATED OXIDATION

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Frictional forces are known to trigger chemical reactions and oxidation of metals through manipulating chemical bonds on a surface. In inorganic materials, understanding the mechanisms and reaction kinetics has been a challenged due to their small molecules. We used a tribochemical approach to conduct in situ study of metal oxidation under friction force. Using this approach, we are able to control the amount of mechanical energy dispersed on a metal surface in a designed chemical environment. Meta-stable oxides were formed. A modified Arrhenius-Eyring equation has been proposed in order to predict the non-equilibrium state of reaction due to friction.

CT–21

MOLECULAR DYNAMICS (MD) SIMULATIONS OF MICROSTRUCTURAL EVOLUTION DURING SLIDING INTERACTIONS

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The high strain-rate, stress, strain and temperature experienced near sliding interfaces suggest that microstructural evolution during sliding nteractions between ductile metals is strongly driven and are the result of several dynamic and interacting phenomena. The aim of this study was to gain insights into these dynamic events via MD simulations. Embedded atom potentials were employed for Fe-Cu, Fe-Ni & Cu-Ni tribopairs to probe the effect of driving force on friction and microstructure evolution in clustering, ordering and miscible binary tribopair systems. Simulations were also conducted on amorphous systems using Lennard-Jones potentials.

The variables included sliding velocity, crystal orientation and defects (for crystalline simulations) and amount of free volume (for amorphous simulations). In both crystalline and amorphous cases, formation of vortices in the vicinity of the sliding interface results in mechanical mixing. Results pertaining to adiabatic and structural flow localization, dislocation and twin activity, nanocrystallization and dynamic recrystallization, vorticity, amorphization and mechanical mixing, material transfer and formation of non-equilibrium phases will be presented. Comparisons with experiments suggest that such simulations can indeed provide valuable insights that are otherwise inaccessible to experiments.

CT–22

MECHANICAL CONTACTS PROBED WITH PICOSECOND TIMESCALE ULTRASONICS AND THERMAL WAVES

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Picosecond ultrasonic or thermal pulses in solids have wavelengths below 100 nm, and are therefore are very sensitive to the state of interfaces. This sensitivity also applies to the presence and nature of mechanical contacts. Measuring the reflection of picosecond acoustic pulses or picosecond timescale thermal waves from contacting interfaces is therefore a promising new line of investigation for characterizing contacts.

We describe an investigation of the contact between a thin chromium film and a silicon nitride ball bearing indenter using an ultrafast optical technique. The area of contact is acoustically imaged to micron spatial resolution using GHz acoustic pulses produced by the ultrashort pulsed optical excitation of the film through a sapphire substrate. In particular, acoustic echoes are detected through transient optical reflectance changes that are monitored by probe optical pulses.

In this way we image the acoustic reflection coefficient at the interface between the film and the indenter. In addition, by imaging the arrival time of the acoustic echoes we determine the penetration profile of the indenter to nanometre resolution and find evidence for plastic deformation of the film. Furthermore, we demonstrate that imaging the transient thermoreflectance gives a different means for measuring the contact area through spatial variations in thermal diffusion.

We thus demonstrate that picosecond ultrasonics and thermoreflectance provide powerful tools for the non-contact evaluation of mechanical contacts with micron lateral resolution. This technique could be applied to the in situ characterization of contact interfaces between machine elements.

TT–13

Friction in Full View

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Friction is a pervasive phenomenon, which is estimated to represent an economic cost of approximately $100 billion/year in the U.S. alone, and an estimated 1.6% of developed countries’ GDP. Although the importance of friction, and reducing it, was recognized as far back as the construction of the pyramids, we still have only a very fragmented basic understanding of the atomic mechanisms. One of the fundamental problems has been the lack of probes to determine what is taking place at the atomic scale at sliding contacts.

We have very recently been able to perform sliding contact experiments using a scanning probe tip *inside* a transmission electron microscope. This allows one to image using the full range of electron microscopy tools what is taking place around the contact region. Some results to date are not over-surprising, for instance the direct observation of a nanoscale graphitic transfer layer when sliding a tungsten tip on graphite [1], as well as electron energy loss data indicating the formation of graphitic material *in-situ* during sliding on very-low friction amorphous carbon films [2]. Some other preliminary observations are less expected, for instance the observation of graphitic wear debris during sliding on graphite with a size which is consistent with an analytic model of sliding via misfit dislocations [3, 4]; the size of the debris is consistent with the stand-off distance for misfit dislocations. Other phenomena have also been observed, for instance “liquid-like” deformation of gold films, similar to the well-known surface diffusion dominated liquid-like growth of thin films [5]; this may partially explain some phenomena in solid-solid lubrication. These and more recent results will be described.

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IT–14

SIZE EFFECTS IN PLASTICITY AND THEIR IMPACT ON CONTACT MECHANICS

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During contact loading all length scales, from nano to macro, are involved in the plastic response of the material and the damage of materials. An overview of the different phenomena controlling plastic deformation at the different length scales will be given. The consequences of the different dislocation structures on the size dependence of strength will be one of the main topics of the presentation. The different types of experimental tools and simulation techniques necessary to describe and analyse these phenomena are discussed. Special attention is devoted to the new micro and nanomechanic techniques, which are developed in the last few years. Both, experimental and simulation techniques will be considered.

IT–15

DISSIPATION IN SINGLE-ASPERITY EXPERIMENTS

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Nanometer-scale single-asperity contacts have been slid over and indented into single crystal surfaces in force microscopy experiments. For atomic-scale movements of the contact, energy dissipation anywhere between zero and several thousand electron volts may occur, the former in cases of superlubric sliding, the latter when a single dislocation is created. We will discuss the different scales and pathways of energy dissipation. In particular, the friction contrast between single layer and bilayer graphene will be discussed in the light of a corresponding contrast of electron-phonon coupling which was discovered by means of angle-resolved photo emission experiments.

IT–16

MECHANISMS OF ATOMIC FRICTION

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Force microscopy is a versatile instrument to investigate physical phenomena on surfaces. The first emphasis is on the study of friction on the nanometer-scale, also called nanotribology. It will be shown that atomic-scale stick-slip is relatively well understood, where the dependence on velocity and normal force is experimentally investigated and interpreted in terms of an extended Tomlinson model. It is essential to include thermal actuation to understand the observed phenomena. The transition from atomic-scale stick slip to continuous sliding will be described [1]. The detailed analysis yields the energy corrugation and the lateral contact stiffness as a function of load. Very low lateral contact stiffness values of the order a few N/m are found. In addition, experiments will be shown to determine the normal contact stiffness, simultaneously. Recently, it has been shown that atomic friction can be controlled with rather high accuracy by electrostatic actuation [2].

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CT–23

MONOTONIC DISSIPATION OF A SIMPLE CONFINED LIQUID

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The solvation force for a liquid under confinement between two surfaces has been widely investigated to help understand processes concerning tribology[1] and biological function[2]. The solvation force, which displays are oscillatory force profile as a function of the separation between the two surfaces, has been measured extensively using both the surface force apparatus (SFA)[3,4] and the atomic force microscope (AFM)[5,6]. With both measurement systems dynamic measurements have been possible, allowing dissipative components of the interaction to be measured in the near surface region. However, in the case of dissipation the results have been far less consistent than for the readily observed oscillatory conservative force profile.

Here we present definitive interaction measurements of a simple confined liquid (octamethylcyclotetrasiloxane) using artifact-free frequency modulation atomic force microscopy (FM-AFM). We establish that the liquid does not exhibit molecular scale oscillations in viscous dissipation when confined, in contrast to previous measurements with the AFM. We also show the qualitative influence on the conservative and dissipative components of the interaction of a phase error deliberately introduced into the measurement, highlighting that artifacts, such as oscillatory dissipation, can be readily observed. Lastly, we explore whether the confinement of water molecules, a biological relevant liquid, shows a similar behavior as the simple liquid, in that the measured dissipation does not exhibit molecular scale oscillations when confined.

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CT–24

A STUDY OF CONSERVATIVE AND DISSIPATIVE COLLOIDAL INTERACTIONS USING MAGNETICALLY ACTIVATED FREQUENCY MODULATION AFM

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The behaviour of fluids in confined geometries has been a topic of great interest in recent times, with particular interest in the role of hydrodynamics in governing the stability of colloidal dispersions which deviate from the quasi-static conditions described by DLVO theory. In such dispersions, which are often highly concentrated, heated, and / or sheared, the collision rate and frequency result in the hydrodynamics (dissipative interactions) dominating over the electrostatic (conservative) interactions. In the pursuit of understanding such systems instrument development in both the SFA[1] and AFM[2, 3] communities has been undertaken in order to allow the simultaneous and independent determination of the relative contributions to the total interaction potential for single particle-particle interactions. These sub-resonance surface modulation techniques have previously been limited in terms of the accessible oscillation frequency and often require extensive calibration to remove instrumental factors from measurements.

Frequency modulation AFM (FM-AFM) utilises a phase locked loop to feedback upon changes in resonant frequency of a driven cantilever due to conservative tip-sample interactions, which can be detected with extreme sensitivity. This ensures that the system is always driven at resonance. In constant amplitude FM-AFM, a second feedback loop controls the oscillation amplitude of the cantilever. The output from this loop is then proportional to the dissipative component of the tip-sample interaction. The conditions of resonant excitation and constant cantilever amplitude allow the formal decoupling of the conservative (electrostatic) and dissipative (hydrodynamic) forces from a single measurement[4]. This technique allows the use of cantilevers with high spring constants without loss of force sensitivity. Magnetic activation is employed to ensure that the mechanical transfer function of the cantilever is free from the influence of the excitation mechanism. This is essential for quantitative analysis.

The application of FM-AFM to colloid probe measurements has allowed the technical limitations of previous studies to be addressed. In addition to the instrumental aspects of the measurement, data will be presented outlining the ability of this novel technique to quantitatively elucidate both the electrostatic (conservative) forces described by DLVO theory and the hydrodynamic (dissipative) interactions both simultaneously and independently. This technique allows high force gradients to be probed reversibly with high sensitivity and does not exhibit the hysteretic behaviour often observed in colloid probe measurements arising from mechanical instabilities.

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CT–25

SURFACE FORCES, RESPONSIVE FILMS AND FRICTION

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Building on our earlier work on the interactions between surfaces bearing films of polyelectrolytes of different structure, we investigate the interactions between responsive films of a pH and temperature responsive polymer pDMAEMA, grafted to gold surfaces. The grafting is performed in situ in a QCM and the responsiveness is similarly monitored by QCM. Both normal and lateral forces are measured in an AFM in colloid probe mode, and the interactions are strongly dependent on solvent conditions. The friction coefficient achieves a maximum value prior to full collapse of the film. In addition, a brief account of the use of repulsive van der Waals forces to remarkably reduce friction will be undertaken.

CT–26

LUBRICATION OF ARTIFICIAL HIP IMPLANTS BY SYNOVIAL FLUID PROTEIN AND GLYCOPROTEIN.

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The effect of individual components and combinations of components of synovial fluid on the lubrication of materials used in artificial hip implants has been evaluated. The adsorption of these components onto the hip implant materials, ultra-high molecular weight polyethylene (UHMWPE) and alumina, has been evaluated by means of fluorescence microscopy. AFM was used to determine the relative effect of proteins and glycoproteins on the lubrication of PE sliding against alumina. The adsorption of components of synovial fluid and the resulting friction behaviour of the materials and lubricants will be presented.

CT–28

ELIMINATING NANOSCALE WEAR

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Endurance requirements in emerging probe technologies, such as probe based data storage and lithography, are extremely demanding. Tip lifetime has been viewed as an unsolved critical issue in this context. For example in probe storage, individual tips serve as both write and read heads, storing data in the form of indentations in a polymer film and sliding over the film during read-back.

In this contribution we first address this issue by discussing nanoscale wear experiments. The system studied is that of a nm-scale sharp silicon tip sliding in contact with a polymer surface under low humidity and with sliding distances up to 1000m. This interface is technically relevant for scanned-probe storage and scanned-probe lithography. We will present our progress in quantifying nanoscale wear processes. The deviations from Archard's wear law can be explained using an analytic model that captures the crucial aspects of wear physics in a quantitative way. The data and model predict that the wear rates found for sliding tips prevent the technical application.

Previously, it has been shown that friction can be controlled by high frequency modulation of the tip-surface force. We have investigated the impact of this technique on tip-wear and media-wear of sliding tips on polymer surfaces. We have demonstrated sliding distances of more than 700m without detectable tip-wear for a sharp tip using high frequency modulation. This appears to be a viable solution for meeting the challenging lifetime requirements to enable scanning probe lithography and data storage.

CT–29

MECHANICAL CHARACTERIZATION OF THIN LAYERS AT THE NANO SCALE FOR TRIBOLOGICAL APPLICATIONS

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Mechanical characterization of thin films and surfaces at the nanometer scale is of a great interest in order to better understand the tribological properties of some thin films. Nanoindentation has become an indispensable method for measuring mechanical properties of small volumes of materials. Though being developed for over than fifteen years, contemporary methods used for nanoindentation are suffering several drawbacks for nanotribological characterization of thin films: -thermal drift of the instrumentation, which limits the measurements of creep properties; -difficult determination of the contact point on soft materials like soft polymers and some solid lubricants.

The present paper introduces a novel ultra nanoindentation method that applies very low loads (from less than 1 µN up to 50 mN) and is capable to perform long term measurement. The method is based on a patented design using active top referencing system and components made from Zerodur® glass to dramatically reduce the thermal expansion of the instrument frame. Several materials including fused silica and DLC were able to demonstrate the very high resolution of this nanoindentation head. The tests were performed mainly at low loads to display the load and displacement resolution capabilities of the instrument. The method is then applied to thin films and soft polymers in order to better understand the mechanical deformation of these materials and the related friction properties under small deformation. By performing nanoindentation tests at low loads, the related friction and adhesion effects in thin films can be evaluated.

The measurements with a hold at maximum load confirmed the extremely low level of instrument thermal drift. This ultra nanoindentation method opens new possibilities of longer term testing for creep determination and polymer evaluation. Its use for the characterization of thin layers of tribological interest is then discussed.

POSTER SESSION

P-1

DIAMOND-LIKE-NANOCOMPOSITE FOR BIOMEDICAL TRIBOLOGY

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Diamond like Carbon(DLC) has been in use as protective coating for wear and friction applications for decades. But the main drawback of DLC is incompatibility with different substrates because of internal stress due to lattice mismatch and thermal expansion mismatch. A novel diamond like coating material has been deposited by plasma enhanced CVD process on different biomedical substrates, viz. SS 316L, Ti-6Al-4V, Co-Cr alloy and UHMWPE. The coating is an interpenetrating network of diamond-like amorphous C-H chains and glass like Si-O chains [1]. Presence of glass like Si-O network makes the coating suitable for almost any substrate material. The deposition temperature is below 200^{o}C and hence the coating can be deposited over polymeric substrates as well. Percentage of Si (5 – 36 at %) in the structure can be varied and hence the nanohardness (17-12 GPa) and tribological behavior (co-efficient of friction 0.08-0.2) can be manipulated. The wear rate is extremely low 1.0×10^{-7} to 1.0×10^{-8} mm^3/Nm. Increase in Si percentage makes the coating soft but the internal stress decreases (0.5-1 GPa) and hence adhesion (30-40 N) to the substrates increases [2-5].

Biocompatibility of the coatings makes it a potential candidate for artificial implants. Generation of UHMWPE wear particles is prime concern for failure of implants. Attempt has been made to give a protective coating on acetabular polyethylene liner and this nano-composite coating is expected to enhance the tribological performance of ceramic ball and UHMWPE cup in a Hip-Simulator.

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P-2

RAMAN SPECTROSCOPY OF MODEL BOUNDARY LUBRICANTS EX SITU AND IN SITU

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Surface-active agents play an important role in lubrication technology and are often used as additives in liquid lubricants films to reduce the friction and wear. Under high loads, in asperity contacts or when there is no relative motion between two surfaces, fluid lubrication breaks down and boundary lubricants are essential to prevent wear and seizure. In other applications where the use of 'thick' films of liquid lubricants is not possible or desirable (i.e. micromotors, hard disk drives), lubrication between contacting surfaces is exclusively in the boundary regime. Despite the use of boundary lubricants in engineering applications for centuries, our understanding of how boundary lubricants work at the molecular level remains unclear. This presentation describes the use of total internal reflection (TIR) Raman scattering to characterise model boundary lubricants both *ex situ* and *in situ*, under realistic conditions of pressure and shear.

The model systems comprise either Langmuir-Blodgett monolayers of long chain fatty acides (such as Zn arachidate) deposited on silica, glass or CaF_2, or phospholipid bilayers fused to a silica surface in water. TIR Raman scattering is a form of vibrational spectroscopy with sub-nm sensitivity and spatial resolution of a few microns. Control of the polarization of the incoming and scattered light allows us to probe the orientation of adsorbed molecules and how that orientation changes under pressure and shear. The resonant frequency and intensity of different molecular vibrations is also sensitive to the packing and conformational order in the lubricant film. Model boundary lubricants are first characterised *ex situ* and then subjected to increasing load in a contact between a ball and a plate. The design of a tribology rig will be described that allows Raman measurements in a sheared contact with simultaneous measurements of friction and load.

P-3

EFFECT OF POLYMER GRAFTING ON THE BILAYER GEL TO LIQUID CRYSTALLINE TRANSITION

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Liposomes prepared from phospholipids along with grafted polymers on the surface are used for potential applications in targeted drug delivery. In this study we investigate the effects of polymer grafting on the phase behaviour of bilayers using dissipative particle dynamics. The bilayer is made up of a single chain containing one head bead and nine tail beads. The polymer is made up of 20 hydrophilic beads and the bilayer is maintained in a tensionless state using a barostat. The bilayer shows a sharp gel (L_β) to liquid crystal (L_α) transition in the absence of the grafted polymer. At a grafting density of 0.25, two additional phases are observed in the L_β to L_α transition. At low temperatures the L_β phase is transformed to the tilted $L_{\beta'}$ phase and upon further increase in temperature the interdigitated phase ($L_{\beta I}$) is observed. The occurrence of the tilted $L_{\beta'}$ phase is accompanied by an increase in the area per head group of the lipid and grafting was found to broaden the temperature range for the L_β to $L\alpha$ transition. Our study shows that the grafting density can be used to control the temperature range and occurrence of a given bilayer phase.

P-4

PROPERTIES OF FUIDS UNDER STRONG CONFNEMENT: A MODE COUPLING APPROACH

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When a fluid is confined between two molecularly smooth surfaces separated by a few molecular layers, it shows an apparent shear viscosity over a million times its macroscopic value and strong shear thinningat remarkablylow shear rates. We extendthemode-coupling theoryofthe viscosityof dense liquids to this case of strong confinement, thus offering a tentative explanation of the growth of viscosity and how it grows as the separation between the surfaces is decreased, and making additional predictions. In our theory, the effect of the walls come through the space dependent static density background, uniform otherwise.

P-5

ADSORPTION ISOTHERMS ON MICA: WATER REDISTRIBUTION AND FILM GROWTH

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Adsorption isotherms of water on muscovite mica are obtained using grand canonical Monte Carlo simulations over a wide range of relative vapor pressures, p/p_0. Three distinct stages are observed in the adsorption isotherm. A sharp rise in the water coverage occurs for $0 < p/p_0 < 0.1$. This is followed by a relatively slow increase in the coverage for $0.1 < p/p_0 < 0.7$. Above $p/p_0 = 0.7$, a second increase in the coverage occurs due to the adsorption of water with bulk-like features. The derived film thickness and isotherm shape for the SPC water model is in excellent agreement with recent experiments of Balmer et al.(Langmuir 2008, 24, 1566). A novel observation is the significant redistribution of water between adsorbed layers as the water film develops. This redistribution is most pronounced for $0.2 < p/p_0 < 0.7$, where water is depleted from the inner layers and film growth is initiated on the outer layer. Potassium hydration is found to play a dominant role in the rearrangement of water near the mica surface. The analysis of structural features, reveals a strongly bound first layer of water molecules occupying the ditrigonal cavities between the potassium ions. In-plane structure of oxygen in the second layer, which forms part of the first hydration shell of potassium, reveals a liquid-like structure with the oxygen-oxygen pair correlation function displaying features similar to bulk water. Isosteric heats of adsorption were found to be in good agreement with differential microcalorimetric data of Rakhmatkariev(Clays Clay Miner. 2006, 54, 402), over the entire range of pressures investigated. Both SPC and SPC/E water models were found to yield qualitatively similar adsorption and structural characteristics, with the SPC/E model predicting lower coverages than the SPC model for $p/p_0 > 0.7$.

P-6

SUBSURFACE DEFORMATION STUDY OF EUTECTIC ALUMINIUM SILICON ALLOY IN WEAR TEST

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Dry sliding wear tests of aluminium-silicon (12%) alloy using a 2mm diameter steel ball show ultramild wear at loads below 500mN. A load of 600mN makes a transition to mild wear. When the load is 600mN the grains in the near surface region undergo a 10 times reduction in size and long silicon particles show incipient fractures and void formation. At higher loads (700mN) the particles fragment to smaller size and the matrix become plastic. The fragmentation continues with increasing loads as the particles flow with the matrix. At very high loads cracks from the particles interface join to give rise to delamination wear. Nanoindentation hardness and elastic modulus of the subsurface, prepared by Focussed Ion Beam Machining, remain unchanged in ultra mild wear regime while hardness and elastic modulus fall continuously when we move towards the edge (within 2-3µm) from the bulk matrix in samples subjected to higher normal loads (700mN & 1000mN). The effect is more significant in 1000mN wear test samples. These show the near surface undergoes large plastic deformation leading to micro/nano void formation which softens the matrix. The resulting damage is severe.

P-7

SURFACTANT TRANSPORT IN OIL-IN-WATER EMULSION TO AID TRIBOLOGY

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To understand the mechanism of lubrication by emulsion, a mixture of oil, water and surfactant, we study the spreading behaviour of water droplet on steel surface under oil (with and without surfactant). The transport of a hydrophilic (high HLB value) anionic surfactant (sodium oleate) in water droplet immersed in oil is contrasted with that of another anionic surfactant (oleic acid), which is lipophilic. Here we find that transportation of surfactant from oil into water droplet is dependent on its solubility in water and a stick-jump type of spreading behaviour of water droplet is driven by the solubility gradient across the oil/water interface. This finding is used to understand the surfactant transportation when a small volume of oil carrying the surfactant, is injected at the top of the water drop surface placed on a substrate. The drop spreads very fast because of lowering of the interfacial tension. We finally relate the adhesion recorded in these experiments with sliding friction experiments carried out in a nanotribometer.

P-8

ATOMIC SCALE FRICTION STUDY OF GOLD SURFACES IN ELECTROCHEMICALENVIRONMENT

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Tribological properties of metal surfaces in electrochemical environment carry significant importance to various scientific and technological applications. A few examples include biological implants, tools and machines in chemical or related industries, electrochemical cells, microfabrication technology etc.

In this study, we report atomic scale measurement of friction on a gold surface in an aqueous perchloric acid environment, using a homebuilt electrochemical friction force microscope. The electrochemical potential of the substrate was alternated during the friction measurements in order to reversibly oxidize and reduce the gold surface. At lower sample potential of 600 mV, the Au(111) surface shows periodic stick-slip behaviour. Switching the substrate potential to 1400 mV leads to instantaneous structural transformation from Au(111) to AuO. The AuO surface shows disordered surface structure and correspondingly, non-periodic stick-slip behaviour. A comparative study of friction, as well as the contact stiffness of the tip-sample junction, was performed as a function of normal load for both surfaces. The structural transition from gold to gold oxide and corresponding change in friction and contact stiffness shows complete reversibility with the applied substrate potential.

In addition, we have also performed electrochemically controlled deposition of copper metal on a gold surface to explore the influence of the monolayer coverage of foreign metals on the tribological properties of the gold surface. Our results demonstrate the range of tribological properties of metal surfaces under electrochemical control.

P-9

THEORETICAL AND EXPERIMENTAL INVESTIGATION OF APPLICATION OF SINGLE-CRYSTAL DIAMOND TIP IN TRIBO-NANOLITHORAPHY

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The recent advances in nanotribology demonstrate potential of the SPM-based techniques that include surface scratching to create 3D nanostructures on the surface. Such techniques became known as tribo-nanolithoraphy [1] and are believed to be successfully implemented in the future nanofabrication industry. An important obstacle to this, however, is the effect of wear at the nanometer scale which is critical to the stability of tribo-nanolithoraphic processes. Such stability is achievable via in-depth theoretical and experimental studies of friction at nanoscale along with the development of pioneering equipment. This work presents the results of theoretical modeling and experimental fabrication of 3D on-surface nanostructures formed by nanoscratching with the use of the multifunctional SPM previously developed by the authors [2]. This instrument is equipped with the pyramidal tip made from boron-doped single-crystal diamond [3]. Molecular dynamics methods were used to model the interaction between pyramidal diamond tip and the scratched surface under the variety of geometrical conditions at different scratching/sliding speeds. Experimental results of the pattering of material structures in nanoscale by using scratching and smoothing with diamond tip are shown.

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P-10

CONTROLLED RELEASE OF ANTI-HIV BIOMIMETIC MICRODEVICE IN GEL FOR INTRA-VAGINAL LUBRICATION AND AIDS THERAPY

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UN global summary of the AIDS epidemic 2007 revealed, women (15.4 million) are approximately 50% of people (33.2 million) infected and living with HIV. In most regions of the world, HIV is affecting women and girls in increasing numbers. As researchers, these statistics emphasize the responsibility and a challenge that include 1. understanding personal risks and responsibilities of our young people to make healthy choices about their sexuality as well as 2. a course for future action. Pursuing this 2nd objective, drug delivery across cellular barriers, such as vagina, is a challenging task. To date, most vaginal drug delivery systems (VDDS) have been formulated as conventional / traditional semi-solid formulations. However, a clear rationale exists for providing long-term, controlled release of anti-retroviral in order to provide continuous protection against heterosexually transmitted HIV infection and to improve user compliance, even during sexual activity. Ideally, a vaginal anti-HIV microdevice in gel should provide intra-vaginal biomimetic lubrication during intercourse, uniform hydrogel-coating of vaginal tissue and retention of this gel layer before intercourse. Most importantly, controlled release of anti-HIV drugs form this microdevice in gel inactivates the viral load potentially introduced during sexual activity, due to increase in effective micro surface area of the therapeutics. Indeed, the simple formulation modification of a gel can lead to enhanced performance of the system containing the same amount of active substances.

In this study, a newer polymeric microdevice (microparticles) in bioadhesive vaginal gel of Zidovudine(AZT) (biological half life of 1.1 hour, 500 mg/day to be given in 2-4 divided conventional oral doses), is developed with improved efficacy, safety and controlled release profiles of the anti-HIV drug, AZT. Initially ethyl cellulose microdevices were optimized and characterized varying different drug:polymer (D:P) ratio. The best ethyl cellulose microcapsules(D: P=1:2) were found for the percent drug content (92.16%), encapsulation efficiency (99.0%), excellent flow properties, FT-IR spectroscopy, scanning electron microscopy (SEM) and *in-vitro* drug dissolution (only 65.07% AZT release, up to 12 hour) studies. The prepared microcapsules were then incorporated in bioadhesive gel prepared using different bioadhesive polymer (2% carbopol 974 was found to be the best). A vaginal anti-HIV microdevice in gel was thus prepared and best gel was found for the percent drug content(74.71%), entrapment efficiency(97.83%), *in-vitro* diffusion studies(AZT release, only15.15%, up to 12 hour) using immediately excised goat vagina and coated model goat vaginal tissue with a stable gel layer with good bioadhesion strength(16.7g), good spreadability (225g/min) and minimum extrudibility (165mg). The drug release kinetics of the developed microdeviced gel were studied. This unique VDDS, with both bioadhesive and sustained release properties, is expected to provide an efficacious anti-HIV therapeutics for lengthier duration. Impeccably, a vaginal anti-HIV microdevice in gel system will be engineered to coat vaginal tissue with a stable gel layer and to release entrapped anti-HIV drug in a controlled fashion in presence of the infecting agent: semen. CONCLUSION: We believe, the further research in this area will fill the gap that other conventional VDDS was not being able to provide and yield technology with significant outcome for the Generation-Next worldwide.

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P-11

STRUCTURE AND DYNAMICS OF DNA-DENDRIMER COMPLEXATION

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At physiological pH, positively charged a polyamaidoamide (PAMAM) dendrimer can effectively bind negatively charged DNA and form a complex structure. Presently the study of this complex formation is of great interest for fundamental (as a model for biological reactions) as well as for practical (as a gene delivery material and probe for sensing DNA sequence) reasons. Here we report the complexation between double stranded DNA and various generation PAMAM dendrimers (G3G5) through atomistic molecular dynamic simulation in presence of water and ions. Stable DNAdendrimer complex is formed on nanosecond time scale. Calculated binding energy of the complexation follows the trend G5>G4>G3 in accordance with the experimental data. To study the effect of dendrimer binding on the structure of DNA various helicoidal parameters are also calculated. We also study the structure of the complex under external pulling force to study the conde nsation decondensation transition.

P-12

IMPLICATIONS OF THE MECHANICAL-DIODE EFFECT ON THE UNDERSTANDING OF NANOSCALE ADHESION AND FRICTION

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When the tip of an Atomic Force Microscopy (AFM) cantilever is in contact with a sample surface, and normal ultrasonic vibration is excited at the tip-surface contact, if the excitation frequency is high enough, or is not coincident with a high-order cantilever contact resonance, the cantilever is not be able to linearly follow the surface vibration due to its inertia. Nevertheless, if the ultrasonic excitation amplitude is sufficiently high that the tip-sample distance varies over the nonlinear tip-sample force interaction regime, the cantilever experiences a quasi-static force during the time that the ultrasonic excitation is acting. This induces a quasi-static deflexion of the cantilever which constitutes the so-called mechanical diode response [1, 2]. The phenomenon has been described by introducing ultrasonic-amplitude-dependent tip-sample force-distance curves [3]. We have further extended the model in [3] by considering the ultrasonic-amplitude-dependent potential energy curves [4]. Those demonstrate that in the case –and only in the case- that energy is dissipated during contact formation and breaking at each ultrasonic cycle, for certain ultrasonic excitation amplitudes, the tip encounters distinct quasi-static minimum-energy states separated by an energy barrier. The quasi-static potential energy landscape for the tip varies as the surface normal ultrasonic vibration amplitude is modified. The excitation of shear surface ultrasonic vibration at the tip-sample contact leads to a lateral mechanical-diode cantilever response which provides information about surface and subsurface shear elasticity, viscoelasticity and friction properties [5]. The activation of a lateral ultrasonic force when increasing the surface shear ultrasonic vibration amplitude causes a reduction of friction at the tip-sample contact. Experimental data on silicon and graphite will be discussed in detail to illustrate these results.

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P-13

ESTIMATING THE SOLUBILITY FACTORS OF ADDITIVES IN AN OIL WATER EMULSION FOR TRIBOLOGY

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In an oil-water emulsion for metal cutting operations various additives with different terminal groups,CH_3, C_6H_5 and also various polyethylene glycol esters, are used. The critical factor involved here for ultimately estimating the frictional properties of these molecules lies in its solubility factors. Here we find the solubility parameters like dispersive force, polar forces of these additives which determine their solubility in an emulsion. The solubility of these additives in oil is determined by the solubility parameters one of which is the interaction potential between the terminal group of an additive and that of oil. We measure this using an Atomic Force Microscope (AFM) and determine the dispersive and polar forces using contact angle studies.

Our objective is to determine the solubility of PEG ester additive in paraffinic,phenolic and napthenic oils. We report this data and comment on the effect of oil conformation on the solubility of this additive and the friction of emulsions made from these three pure oils. The frictional studies were carried out in a nanotribometer.

P-14

NANOTRIBOLOGICAL CHARACTERISATION OF HUMAN HAIR BY FFM UNDER AQUEOUS CONDITIONS

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The tribological properties of human head hair have been measured using friction force microscopy (FFM). Hairs were immobilised by embedding them in indium. The friction force was measured as a function of the applied load, both in air and also under phosphate buffered saline solution. A linear friction-load relationship was observed and coefficients of friction compared for virgin and damaged hair. Hairs were damaged chemically, by immersion in potassium hydroxide solution. Samples treated with conditioners were also characterised. The distribution of the conditioner was measured, and large accumulations observed near cuticle edges. The coefficient of friction was also measured for the conditioner treated hair.

P-15

OBSERVATION OF DEFORMATION IN TiN/ TiALN COLUMNAR MULTILAYER COATING

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Nitrides are important class of wear resistant materials used as thin film coatings on the structural materials. It is a well known fact that thin films have improved properties over the bulk material. TiN and (Al,Ti)N are important Nitrides which have shown excellent wear properties, oxidation resistance and also an appealing metallic lusture. With the present trend which is moving towards making multilayer films of the nitrides which are known to have much higher wear properties while having little change in hardness compared to their component monolayer films. The contact deformation studies provide information regarding the mechanism of sub-surface deformation which is valuable inputs in wear studies. It is seen that TiN/(Al,Ti)N multilayer films to about 11% compression and also bending in the layers up to 0.45 times the thickness of film in 130nm and 350nm bilayer multilayer. It is a very surprising to see so much plasticity in these materials as they are highly brittle. It is found to be definitely because of the presence of interfaces as the extent of bending varied with bilayer period. So in order to know more about the bending and how it changes with thickness of the film indentations were made at different thicknesses to obtain the load displacement curves. The indentations cross sections were prepared using FIB to see the sub-surface deformation. The indentation curve and the subsurface deformation were analyzed together. It is seen that the normalized extent of bending of layer does not depend on thickness and the indentation depth. Also the mechanisms for inclined cracks and lateral cracks were studied analytically. Also TEM cross sections were prepared to understand the microscopic details of the deformation modes. It confirmed the presence of bending of layers but no bending of columns was seen. It also shows the formation of micro-cracks at the boundary between the bent layers and the sheared columns inside the film which act as precursors for inclined cracks and lateral cracks.

P-16

LUBRICATION REQUIREMENT OF GEARBOX IN WINDMILL

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Windmills are the most popular alternative system of power generation in current energy crisis scenario., due to very low energy cost. Though the initial cost is higher but in long run these are very cheap system. The windmill gearbox can generate upto 600 KW of wind power. The gearbox are speed increaser type, suitable to transmit the power generated by windmill at about 20-23 rpm. The gearbox used to increase the speed from 20 rpm to 1500 rpm. Since gearbox is located at height, frequent lubrication is very difficult and costly affair. Therefore lubrication of gearbox is very important that contributes to reliability of functioning and long service intervals. Due to unreliability of wind the gearbox encounters to shock loading in addition to regular load. Additionally, the gearbox need to support the power generator and disc brake and wind turbine blades through hexagonal flanged low speed shaft. Therefore lubrication requirement of gearbox is very crucial to run the windmill. Considering the severity of operating conditions of gearbox in windmill, we have attempted to develop an open gear lubricant for gears of wind mill. To achieve the high load carrying property we have studied nano particle size Molybdenum Disulfide in open gear lubricant. The developed open gear lubricant was tested for various parameters in laboratory including performance tests. The product has shown high load carrying properties as evidenced by higher weld load and Timken OK load. After getting encouraging results in laboratory the product was subjected to field trial in wind mill.

P-17

INTERACTIONS BETWEEN GRAFTED POLYMER BRUSHES IN AN AQUEOUS ENVIRONMENT

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Surface-bound, brushlike copolymers can be used as effective surface coatings for improving both the protein resistance and lubrication properties of surfaces. In these applications, the ability of the polymer-brush layers to bind solvent molecules in a surface layer is highly important. Using the surface forces apparatus (SFA), we have investigated the interactions between water-soluble brush-forming polymers grafted onto a PLL backbone, such as poly(L-lysine)-g-dextran (PLL-g-dex) and poly(L-lysine)-g-poly(2-methyl-2-oxazoline) (PLL-g-PMOXA), adsorbed on mica in an aqueous environment. We measure the interaction force as the brushes are compressed under a normal load. The refractive index of the compressed film is simultaneously measured, from which the amount of polymer adsorbed on the mica surface can be extracted. Comparing surface force isotherms, taken at a range of temperatures, with scaling theory allows for a measurement of the distance that the polymers extend into the solvent (that is, the brush length *L*). We thus evaluate the load-bearing ability of the brushes as a function of the solvent quality.

P-18

EFFECTS OF SURFACE MORPHOLOGY ON ADHESION AND FRICTION

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All surfaces are rough on the nanometer scale and the effect of roughness has attracted increasing interests in the nanotribology field. An important consequence of this roughness is that the actual area of contact is much smaller than the apparent contact area, true solid-solid contact occurs only between surface asperities. To model this roughness, we have employed a nanoparticle gradient substrate to study effects of roughness on adhesion forces between two surfaces. Moreover, it is known that the adhesion (and adhesion hysteresis) between two surfaces in contact plays an important role in determining the frictional forces when lateral sliding is initiated. Using the atomic force microscope (AFM) we have measured the adhesion and friction forces between a colloid probe and a morphological gradient surface. This approach allows for force measurements in which the surface roughness can be varied systematically while keeping all other experimental parameters constant and exploring the relationship between adhesion and friction on the nanometer scale.

P-19

LUBRICATION AND SURFACE PROPERTIES OF ROACH CUTICLE

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Using atomic force microscopic and tribometry techniques, we characterized the cuticle surface of the American Cockroach (Periplaneta Americana) and studied lubrication properties of the wax developed to protect the cuticle. Experimental results showed that the roach cuticle had the ability to self-clean and there were dimples on its surface to naturally disperse was. It was observed by changes in friction, that a thicker layer of wax was formed at the ventral abdomen, where dimples were present, that at the dorsal abdomen which was absent of mayor features. The wax was found to have similar lubrication properties as commercial automobile oil, but with the ability to form thin films and repel dust. The dust repelling qualities make it a potential candidate for lubrication of MEMS and NEMS devices that require cleaning surfaces that is cost effective.

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EFFECTS OF SURFACE MORPHOLOGY ON ADHESION AND FRICTION

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All surfaces are rough on the nanometer scale and the effect of roughness has attracted increasing interests in the nanotribology field. An important consequence of this roughness is that the actual area of contact is much smaller than the apparent contact area, true solid-solid contact occurs only between surface asperities. To model this roughness, we have employed a nanoparticle gradient substrate to study effects of roughness on adhesion forces between two surfaces. Moreover, it is known that the adhesion (and adhesion hysteresis) between two surfaces in contact plays an important role in determining the frictional forces when lateral sliding is initiated. Using the atomic force microscope (AFM) we have measured the adhesion and friction forces between a colloid probe and a morphological gradient surface. This approach allows for force measurements in which the surface roughness can be varied systematically while keeping all other experimental parameters constant and exploring the relationship between adhesion and friction on the nanometer scale.