

The Photochemistry, Structure and Dynamics of Delocalized Charges in Organic Thin Films

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Abstract

The talk will describe the investigation of radical cations in organic thin films, including conjugated polymers, liquid crystalline derived films, and aromatic single crystals. The charges are investigated by a novel nanometer scale electrostatic ion trap methodology based on a near-field scanning optical microscope. Ions are detected indirectly via ion induced fluorescence quenching. The technique allows for measurements of ion mobilities and ion concentrations at chosen locations in a thin film sample including a functioning organic electronic device, e.g. LED. The method offers the opportunity to correlate ion densities and dynamics with the structure of the film. The latter is determined simultaneously by near field scanning optical microscopy and topographic shear force measurements of the sample under investigation. Applications of the technique to key model devices will be described.

Instabilities in dynamic force curves

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Abstract

The intermittent-contact mode of atomic force microscopy has proven very useful for weakly adhered samples, for viscous samples, and for providing high contrast in phase images between different materials. However, understanding the data has proved to be more challenging and interesting due to the extremely nonlinear tip-sample interaction throughout an oscillation cycle. Ramping the sample position as the cantilever is oscillating, and observing its amplitude and phase as a function of position is called dynamic force spectroscopy. An understanding of these data is instrumental to interpreting intermittent-contact mode images. As in regular quasi-static force-curve acquisition, the tip feels a potential due to the spring-like behavior of the cantilever beam, plus the potential of the tip-sample interaction. The instabilities in quasi-static force curves ("snap-in" and "snap-out") as well as the sudden jumps in amplitude and phase in dynamic force curves originate in the changing shape of the total potential.

Fourier analysis in nanoshear modulation of polymers

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Abstract

We have developed a low-frequency shear-modulated probe of polymers, based on a modified atomic force microscope utilizing Fourier analysis of nonlinear response. The technique is uniquely sensitive to the onset of plastic deformation in the nanometer

regime manifest as creep. We present a methodology for data analysis that identifies and separates elastic and creep response. Fourier analysis of creep response is much more sensitive to the onset of wear than subsequent topographic image analysis. Parameters governing the onset of wear were examined in polystyrene films varying in molecular weight; the importance of entanglement was identified. The methodology was applied to examine an interface between poly(methyl methacrylate) and poly(acrylonitrile). Whereas this miscible system exhibits zero contrast under conventional force microscopies (force modulation, friction force, phase imaging), Fourier-analyzed shear modulation response unveils a continuous transition across the interface. This suggests the ability to probe interdiffusion and entanglement with resolution below 100 nm.

AFM study of capillary wave fluctuations on - and spinodal dewetting of thin polymer films

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Abstract

The natural roughness of thin polymer films was characterized by IC-AFM. Polystyrene and poly(vinyl pyridine) spin-coated films with thickness ranging between 1 to 16 times R_g were annealed for various times well above T_g and quenched to room temperature. Different molar masses were used to probe the ratio of film thickness to R_g . The power spectral density was determined from images obtained at different cell sizes. These results show that the free surface of polymer melts follows laws of capillary wave fluctuations as do surfaces of low molar mass liquids provided films are thick enough. Thinner films are unstable or metastable depending on the absolute thickness of the film and not the molecules confinement. Unstable films present the amplification of selected spatial frequencies in the roughness spectral density which is most likely the manifestation of spinodal dewetting. Metastable films dewet by the classical mechanism of nucleation and growth of holes.

Dynamic force spectroscopy for drug design

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Abstract

The application of dynamic force spectroscopy (DFS) in rational drug design is demonstrated in a study of the interactions between streptavidin, its natural ligand biotin, and two biotin derivatives. The force spectrum for the 2' enantiomer is identical over the timescales probed, revealing that the interactions measured are a consequence of bonding to parts of the molecule away from this chiral centre. This conclusion is supported by experimentation using iminobiotin that has less hydrogen bond propensity at the head-group, away from the 2' carbon tail.

Atomistic simulations can reveal the origins of the interactions measured by DFS. However, the disparity in timescale between that of the laboratory and of the computer causes a significant problem with six orders of magnitude difference in time between reality and simulation. Clearly current simulations are of little relevance to the study of thermally driven molecular interactions. A development of stochastic action dynamics offers hope in the simulation of molecular transitions under force. Married to new developments in high performance computing these new simulation strategies should open the door to routine microsecond-plus simulations.

Imaging charge in organic thin film devices by variable-temperature electric force microscopy

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Abstract

We are investigating organic thin film transistors by variable-temperature electric force microscopy (EFM). A long-standing question concerning the behavior of organic devices is the nature of interfacial charge traps and their relation to mobility in disordered material. Improvement and understanding of organic transistor performance relies on our ability to characterize charge traps at the buried semiconductor/dielectric interface. By quantifying charge-trap energies, correlating their location with surface morphology, and observing their dynamics we can begin to infer the chemical nature of the traps. We will discuss ongoing work employing cryogenic electric force microscopy to image buried charge in organic devices.

Entropic barriers in nanoscale adhesion studied by variable temperature chemical force microscopy

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Abstract

Intermolecular forces drive a variety of phenomena in biological systems, such as cell adhesion, protein folding, and molecular recognition. Modern ultra-sensitive force microscopy techniques enable direct measurement of the chemical bond strength. Still, little is known about the bond strength response to the changes in temperature, despite the fact that it provides a direct way to determine thermodynamic characteristics of the interaction. We used an atomic force microscope (AFM) to measure the temperature dependence of the interaction forces in a well-defined system presenting a finite number of identical interactions between the force microscope tip and sample surface. The tip of the scanning probe microscope was modified with distinct chemical functionalities to alter the chemical nature of the interaction. We measured interaction forces between

different tip-sample functionalities as a function of temperature in a series of solvents and solvent mixtures. We will discuss the results of our measurements as well as the theoretical framework for their interpretation based on the kinetic model of bond dissociation. We will focus on the interplay of thermodynamic and kinetic factors affecting the bond strength in the presence of solvent medium, specifically on the entropic contributions to the interaction strength.

Mechanical and electric properties of alkyl monolayer formed on Si(111) via Si-C bond studied by current sensing AFM

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Abstract

Electric properties of alkyl monolayers with different chain-lengths covalently bonded directly on an n-type silicon (111) semiconductor have been evaluated by using current sensing atomic force microscope (CSAFM). The alkyl monolayers were constructed on a hydrogen terminated silicon substrate by immersing the substrate in the neat $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{CH}_3$ ($n=12, 14, 16$ and 18) liquid at 200 degree. The current across the monolayers showed strong force and alkyl chain-length dependencies. The current-voltage (I-V) dependencies were analyzed with the thermionic emission mechanism corrected by tunneling. From the chain-length dependence of the I-V curves, the tunneling coefficient of 0.64 \AA^{-1} was derived. The mechanical properties of the monolayers were also evaluated by analyzing the force dependent electric properties of the monolayers.