Laboratorio de Ciencias de Superficies y Medios Porosos

Workshop on
Molecular and Particle Processes at Solid Surfaces
San Luis, 15, 16, 17 November 2004

INVITED TALKS PROGRAM

November, Monday 15  Time: 11:00  Chairman: Dr. Félix Nieto

Enantioselective Chemisorption on Chirally Patterned Surfaces in Ultrahigh Vacuum

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The enantioselective chemisorption of S- and R-propylene oxide is measured in ultrahigh vacuum on a Pd(111) surface chirally patterned using S- and R-2-butanol. RAIRS reveals that adsorbed 2-butanol forms 2-butoxide species on Pd(111) when heated to ~150 K, converting to a ketone with concomitant loss in chirality at 200K. Propylene oxide adsorbs reversibly on Pd(111) at 80K without undergoing any thermal decomposition thus providing an ideal probe of surface chirality. It is found that the coverage of R-propylene oxide adsorbing on an R-2-butoxide modified surface, ratioed to that on one covered by S-2-butoxide, reaches a maximum value of ~2 at a relative 2-butoxide coverage of ~25% of a monolayer. Enantioselectivity is lost when the surface is patterned using 2-methyl butanoic acid. Here the chiral center is identical to that in 2-butanol, but is now anchored to the surface by a carboxylate group. The enantioselectivity is restored when using 2-amino butanoic acid as a modifier, and the loss of enantioselectivity for the carboxylic acid is ascribed to a loss of rigidity of the chiral center, which allows it to azimuthally rotate. Rigidity is restored by functionalization with an amine group. The enantioselectivity of a Pd(111) surface modified by a series of amino acid is explored, where it is found that the enantioselectivity decreases slightly with increasing alkyl chain length, but decreases to zero for branched alkyl chains. In all cases, the enantioselectivity varies with modifier coverage showing a peak enantioselectivity at 25 to 33% of saturation coverage. Similar experiments were carried out using 1-(naphthyl) ethylamine (NEA) as a modifier and propylene oxide as a probe, where no enantioselectivity was found. Enantioselectivity is restored when 2-butanol is used as a probe, an effect that is ascribed to a stronger interaction between NEA and 2-butanol. In this case, the enantioselectivity reaches a maximum when flat-lying NEA saturates the surface, and decreases as the adsorbed NEA tilts.
Fractional Statistical Theory of Adsorption of Polyatomics

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The basis of a fractional statistical thermodynamic theory of adsorption (FSTA) of polyatomics are presented from a new conceptual framework inspired in the formalism of Haldane’s statistics recently developed on a generalization of the Pauli’s Exclusion Principle[1]. The theory is characterized by an exclusion parameter $g$ related to the configurational entropy and consequently to the configuration of the admolecules and surface geometry. A simple approach to a complex problem is thus obtained as well as the parameters of the theory are related to physical properties of the system accessible from experiments[2].

It is put forward in this paper that adsorption of structured gases can be treated within a generalized statistics with a statistical exclusion parameter $g>1$. A description emerges from which not only the adsorption heat, but the spatial configuration of the molecule in the adsorbed state can be obtainable through thermodynamic data. The advantages of using this description as a tool for interpreting polyatomic adsorption data and for characterization of the adsorption potential is shown by analyzing simulation results in lattice gases as well as experimental adsorption isotherms of various adsorbates. Additionally, a novel method (thermodynamic configurational spectroscopy) is introduced to investigate the changes of adsorbate’s configuration upon density increasing from thermodynamic data.

methods have demonstrated the ability of these surfaces to differentiate between enantiomers of molecules adsorbed on them. Theoretical and experimental efforts to create surfaces of this type by epitaxial deposition of thin metal films on metal oxide substrates will also be presented. A second route to endowing metal surfaces with chirality is to adsorb chiral molecules onto otherwise achiral surfaces. The formation of ordered adlayers of amino acids on flat metal surfaces is one example of this approach that has been widely studied experimentally. We have used Density Functional Theory calculations to resolve several experimental controversies regarding the structure of amino acid adlayers on Cu surfaces and to investigate whether chiral domain segregation can occur when racemic mixtures of amino acids are present on these surfaces.

November, Monday 15 | Time: 15:15 | Chairman: Dr. Víctor Pereyra

**Some examples of the adsorption of molecules on oxide and metal/oxide catalysts studied using all-electron first-principle methods**

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Usually oxides are used as a supports for catalytic metallic active phases. Besides oxides show acidic and basic sites in their surfaces, making possible the formulation of catalytic reaction pathways for a large variety of chemical reactions, including hydrogenations, dehydrogenations and oxidations. The existence of structural defects on the surface of oxides seem to play a key role in several processes where adsorption and surface reactions take place. In the case of rather inert systems as the (100) face of MgO, these defects fully define its reactivity in dissociative processes.

The study of atomic and electronic properties of these surfaces by calculating optimized geometries, interaction and reaction energies, vibration frequencies, atomic net charges and charge and spin spatial density distributions has become a valuable tool in the understanding of the catalytic processes. For that purpose are essential an adequate model for the reactive site and the use of high quality computations based on all-electron first-principle methods. At the present, one of the most precise formalisms is the Density Functional Theory (DFT).

In this talk, the adsorptive properties of magnesium oxide (MgO) and gallium oxide (Ga2O3) interacting with methanol molecules are shown, particularly when defects are present. On the other hand, the adsorption of NCO- and HNCO species on Cu/SiO2 and of NO, NO2, N2O2 species on BaO have been considered, all of them of interest for removal of pollutant gases from vehicle exhausts.
Low-dimensional phase transitions in the confined Ising Magnet

Ezequiel Albano

INIFTA. Universidad Nacional de La Plata

When a magnetic Ising film is confined in a LxM geometry (L << M) and competing magnetic fields (h1) are applied at opposite walls along the M-direction, a localization-delocalization transition of the interface between domains of different orientation that runs parallel to walls, can be observed. This transition is the precursor of a wetting phase transition that occurs in the limit of infinite film thickness (L → ∞) at the critical curve Tw(h1w).

For T < Tw(h1) (T > Tw(h1)) such an interface is bounded (unbounded) to the walls, while right at Tw(h1) the interface is freely fluctuating around the center of the film.

We present extensive Monte Carlo simulations of Ising stripes in the LxM geometry, in order to describe both the localization-delocalization transition and the properties of the delocalized interface. We make use of a suitable algorithm to define the local position of the interface along the film, such that its probability distribution can be used to account for of the transition itself and the fluctuations in the local position of the interface (capillary waves). After describing the interface localization-delocalization transition, we pay attention to the properties of the delocalized interface with an emphasis on the effects of confinement.

Discretized model for a chain diffusion in one dimension

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The one-dimensional diffusion motion of a chain of N beads is studied with the help of a Monte Carlo simulation. We show that the scaling exponent for the viscosity can be smaller or greater than 3 but it scales as N³ in the asymptotic regime (N→∞). This anomalous behavior cannot be attributed to the diffusivity scaling or the length fluctuations but is due to the chain dynamics details during diffusion in which the end beads play the key role. The model is extended to study the diffusion of chains in microporous solids. The difficulties a chain has to escape from a pore where it is confined is found to strongly depend on the ratio between the chain length and the cage size. We found a window effect that can be explained without using any energy argument.
Incidence of Polymeric Structure on Ionic Transport

Marta Rosen
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Systematic experiments of ionic transport in scleroglucan solutions have been performed. The concentration range covered from dilute solutions to gels. Previously the critical concentration of each regime was determined. Ions belonging to the IA and IIA groups of the Periodic Table, in increasing size, have been chosen.

In order to obtain diffusion coefficients, two methods have been used. Working each concentration alone shows drastic changes that coincided with the critical concentration previously determined. For diluted solutions and gel, the obstruction and obstruction-tortuosity models are in agreement. But, for semi-diluted solutions specialized hypothesis and numerical simulation to show structural transformation and ion-polymer interaction were required.

Improvement on Electrocatalysts for Direct Methanol Fuel Cells

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The anodic electrooxidation of methanol in Direct Methanol Fuel Cells is a complex process, involving 6 e- per molecule, which requires of high efficient electrocatalysts due to the low working temperature (<100°C). Carbon supported PtRu catalysts are commonly employed. However, the improvement of these electrocatalysts is an essential goal in the development of practical methanol fuel cells. The use of carbon black as support for noble metals is frequently employed in the electrodes of polymer membrane electrolyte fuel cells, but the impact of the chemical and physical properties of the carbon on the electrocatalytic performance are not yet sufficiently understood. The presence of surface oxygen influences the surface behaviour of carbons to a great extent, and the role of oxygenated functionalities on the formation of the dispersed platinum is well recognized, but not with an additional metal like ruthenium. The use of an appropriate method for the formation of nanoparticles in the presence of
the carbon black, and the surface modification of this support, improve the behaviour of the PtRu supported electrocatalysts, as it can be followed by cyclic voltamperometry and cronoamperometry.

November, Tuesday 16 Time: 11:00 Chairman: Dr. Karim Sapag

Mechanistic Aspects of the Structural Characterization of Porous Solids by N2 Sorption and Hg Porosimetry

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A study about several mechanistic and phenomenological aspects of mercury intrusion and nitrogen sorption processes occurring inside model and real mesoporous systems is undertaken. The experimental pore systems include two substrates: a globular solid made of monodisperse silica spheres in a perfect rhombohedral arrangement and a controlled porous glass solid. Analysis and comparison between N2 sorption and Hg porosimetry pore-size distribution results provide evidence about important features such as: (i) the identification of several types of mechanistic aspects which are responsible of irreversible capillary behavior, thus influencing the calculation of pore structural parameters; (ii) the choice of the right sorption process (i.e. condensation or evaporation) that is suitable for comparison with either mercury intrusion or extrusion results; (iii) the types of porous structures which are liable of a convenient pore-size characterization by either N2 sorption or mercury porosimetry methods; and (iv) the nature of the pore entities (i.e. sites or bonds) that assume control of the capillary processes.

November, Tuesday 16 Time: 11:45 Chairman: Dr. Karim Sapag

Cu+ and Ag+ dispersion on mesoporous silica SBA-15

Elena Basaldella
CINDECA, La Plata

Recently, the adsorption properties of SBA-15 for the separation of commercially important light hydrocarbons were tested. It was demonstrated that the SBA-15 framework possesses a higher affinity for the alkenes than the corresponding alkanes. Despite the fact that no metal cations are present in this structure, it was noted that this behaviour was in line with those observed on π-complexation systems. Besides, previous studies performed in our laboratories demonstrated that SBA-15 mesoporous materials containing Cu or Ag cations can be used as an effective adsorbent for propylene/propane separation. The presence of metal cations in the adsorbent lattice led to a greater selectivity towards propylene. Although the metal-containing samples showed a higher capacity for propylene, the methodology used for cation incorporation was not studied in detail. On the other hand, the adsorbents prepared by us usually consisted of an active component dispersed on a support, with a high specific surface, being the dispersion produced by a careful controlled heat-treatment. On these basis, the
present work studies the effect of heat treatments on nature and dispersion of Cu and Ag species on SBA-15 type materials. The samples were characterized by XRD, TPR, SEM, TEM, XPS and N₂ adsorption.

November, Tuesday 16  Time: 14:30  Chairman: Dr. José Ramírez

Numerical methods for bond and site percolation

Eugenio Vogel

Universidad de La Frontera, Temuco, Chile

After a short introduction to the percolation problem, the cases of bond and site percolation in two dimensions are tackled. The technique of progressive percolation trajectories is introduced and applied to square, triangular and honeycomb lattices. The aim is two-fold: to obtain percolation thresholds and critical exponents as the size of the percolation cell increases. Comparison with analytic expressions valid in the thermodynamic limit is performed to validate percolation trajectories as an approximate numerical method. This will allow its application to inhomogeneous systems, where analytic expressions are not possible.

November, Tuesday 16  Time: 15:15  Chairman: Dr. José Ramírez

A topological explanation for the glassy behavior observed in the Mean Field Hamiltonian model

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In this work we use a topological approach to explain the origin of the quasi stationary solutions of the Mean Field XY Hamiltonian model. We verified, by means of numerical simulations that the system, when initially prepared in a water bag configuration, is rapidly trapped into a trajectory along which the system visits, on after another, a set of isolated saddle points with a relatively large number of unstable directions. This dynamical behavior somehow resembles that observed in supercooled liquid above the mode coupling temperature T_C.
Diffusive mixing of grains: some experimental results

Irene Ippolito
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We report some experimental studies of the diffusive properties of bidisperse flows of grains and discs and monosize flows of grains of different densities, moving under gravity through an array of obstacles. These experiments have been performed in 2D and 3D arrays. In 2D, the experimental set-up consists in a vertical hexagonal array of obstacles, i.e. Galton Board; in 3D, the experimental set-up consists in a number N of steel squared grids, placed parallel to the floor. In some cases, the separation between grids e has been varied. During the fall, particles collide with the obstacles of the array (or the grids), spreading them in aleatory directions. As a consequence, the initial flow of beads can be dispersed and the motion of the particles decorrelated. Eventually, a diffusive regime can be achieved. At their exit from the array, the beads accumulate orderly in discrete collectors. Afterwards, the final mass distributions of the beads are reconstructed. These distributions permit to determine a degree of mixing, as well as the dispersion lengths that characterize the spreading amplitudes for the different diameters of the particles or densities.

Slow dynamics and the supercooled tetragonal-liquid state in ultrathin magnetic films

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The competition between anisotropy, ferromagnetic exchange interactions and dipolar interactions in ultrathin metal-on-metal magnetic films generates very complex and rich behaviours in both its equilibrium (i.e., thermodynamical) and non-equilibrium properties. In particular, at low enough temperatures the magnetic moments undergo a reorientation transition, where they become oriented perpendicular to the plane of the film, but the magnetic order is lost. In this situation, the physics of the system can be well described by an Ising model with competing short range ferromagnetic interactions and long range antiferromagnetic interactions that decay as $r^{-3}$ with the distance between spins. Further decrease in the temperature leads to the appearance of a laberynth structure with four-fold simmetry (the so called "tetragonal liquid state"), which undergoes a phase transition into a striped state, which results from the frustration of the microscopic interactions. Using Monte Carlo simulations and some analytic calculations on a continuum version of this model we show that this is a weak first order phase transition. Moreover, this lead to the posbility of having a supercooled metastable tetragonal liquid state below the melting temperature. Using numerical simulations we analize the stability of the supercooled state showing that, after a quench from intemediate temperatures, the system may relax into the stable (striped) state through two different mechanisms: coarsenig or decay into the metastable state followed by a
nucleation process. This method allows an estimation of the free energy barriers that govern the nucleation process, showing that the supercooled state remains stable even at very low temperatures.

November, Wednesday 17  Time: 9:00  Chairman: Dr. José Marchese

**On the application of computer simulations to the study of electrochemical nanostructuring and surface phase formation**

Ezequiel Leiva  
Universidad Nacional de Córdoba

In the present talk we review some of our recent work on computer simulations devoted to understand different aspects of electrochemical nanostructuring and surface phase formation. We give a short introduction on the most common experimental techniques employed for electrochemical nanostructuring, discussing the status of theoretical modeling for them. Then, we analyze the application of atom dynamics and different types of Monte Carlo simulations to the present problem.

November, Wednesday 17  Time: 9:45  Chairman: Dr. José Marchese

**Application of the AFM to the Structural Characterization in Separative Membranes**

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Atomic force microscopy (AFM), is a characterization technique which presents high possibilities of application in the field of materials. A small tip scans the surface and moves vertically according to its interaction with the sample. In AFM the tip is placed on a cantilever whose deflection can be detected by the reflection of a laser beam appropriately focussed. This allows to analyse non conducting materials, what makes the method more convenient to study membrane materials.

Several operation procedures can be used in AFM: Contact, Non-contact and Tapping or intermittent contact mode AFM. These techniques give account of the sample topography. Moreover, other properties of the surfaces can be obtained, by analyzing different forces between sample and tip. For example, the phase contrast provides information about differences in surface adhesion and viscoelasticity. Magnetic and electric force microscopy, both measure magnetic (or electric) force gradient distribution above the sample surface. Surface potential microscopy measures differences in local surface potential across the sample surface. Force modulation measures relative elasticity/stiffness of surface features and lateral force microscopy analyzes the frictional force between the probe tip and the sample surface. In many of these techniques, appropriate treatment of the measured forces is necessary to eliminate the contribution of the topographical images.