Surface Science
Session Chair: Ilan Goldfarb

Keynote 1: **Edward Bormashenko (Ariel University)** Quantification of Ordering in 2D Patterns
Keynote 2: **Moshe Ben Shalom (TAU)** Ladder Ferroelectrics by vdW Sliding

Invited 1: **Beena Kalisky (BIU)** Imaging quantum materials with scanning SQUID microscopy
Invited 2: **Igor Rahinov (Open U)** Steric hindrance of NH_3 diffusion on Pt(111) by co-adsorbed O-atoms

Contributed 1: **Adva Ben-Yaacov (WIS)** On the interaction of hydrogen with ceria in ambient conditions: hydride formation VS hydroxylation of the surface

Contributed 2: **Alexandr Leontev (Technion)** Analyzing and modeling of microrheological and adhesive properties of soft hydrated surfaces by AFM and flow cell tests

Contributed 3: **Tatyana Bendikov (WIS)** Charge Transport across Biomolecular Electronic Junctions. Ultraviolet and X-ray Photoemission Spectroscopy Studies

Quantification of Ordering in 2D Patterns

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Quantification of ordering in 2D patterns is discussed. A continuous measure of symmetry and the Voronoi entropy of the diversity of 2D patterns is discussed [1-2]. A continuous measure of symmetry and the Voronoi entropy of patterns representing Voronoi diagrams emerging from the Penrose tiling were calculated. Voronoi diagrams emerging from the centers of the edges of the Penrose rhombs, considered as nuclei, deny the hypothesis that the continuous measure of symmetry and the Voronoi entropy are always correlated. The Voronoi entropy of this kind of tiling built of asymmetric convex quadrangles equals zero, whereas the continuous measure of symmetry of this pattern is high (see Fig. 1) [2].

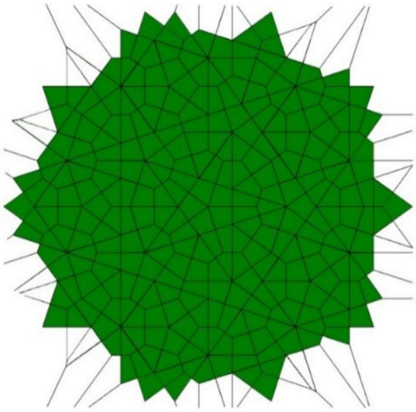

Fig. 1. Voronoi diagram emerging from the Penrose Tiling P3. Centers of the edges of Penrose rhombs are taken as the seeds. The Voronoi entropy is zero; continuous measure of symmetry is high.

Informational (Shannon) measures of symmetry are introduced and analyzed for patterns built of 1D and 2D shapes. A continuous measure of symmetry and the Voronoi entropy of capillary clusters is treated.

[1] Ed. Bormashenko, I. Legchenkova, M. Frenkel, N. Shvalb, Sh. Shoval, Appl. Sci. **12** (3), 1127 (2022).
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Ladder Ferroelectrics by vdW Sliding

M. Ben Shalom, School of Physics, Tel Aviv University

We demonstrate and study a polar layered system with distinct ladder-like polarization steps that accumulate with each extra atomic layer. Moreover, the symmetries of these diatomic crystals translate planar shifts by one interatomic spacing to the out-of-plane switching of the structure and its polarization. I will discuss the origin of this ultimately thin interfacial polarization, the unique cumulative response at the atomic limit, the robust co-existence with in-plane conductivity, and the switching dynamics observed in our experiments and modeled by our first principle calculations.

"Interfacial ferroelectricity by van-der-Waals sliding"

https://www.science.org/doi/10.1126/science.abe8177
https://arxiv.org/abs/2010.05182

“Cumulative Polarization in Conductive Interfacial Ferroelectrics”

https://www.nature.com/articles/s41586-022-05341-5
https://arxiv.org/abs/2206.12215

Imaging quantum materials with scanning SQUID microscopy

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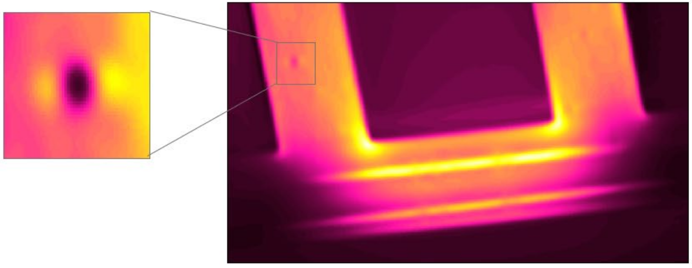
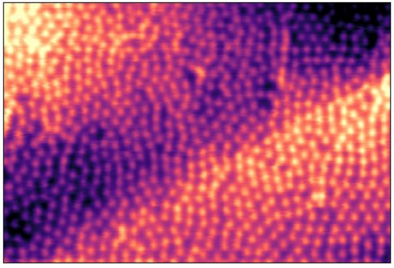
Competition or cooperation between different electronic orders with similar energy scales often gives rise to new or unexpected behaviors. Detecting traces of such orders requires versatile probes, which can probe different aspects of the system, such as conductivity, superconductivity and magnetism. In my talk, I will describe two systems where our local view uncovered surprising mesoscopic effects. In the oxide interface $LaAlO_3/SrTiO_3$, we imaged the current flow close to a metal-insulator transition. We found that the critical behavior is controlled by structural domain patterns in the substrate, rather than by universal scaling laws. In the transition metal dichalcogenide 4Hb-TaS_2 we show that the superconducting state hosts a spontaneous vortex phase, where vortices appear in the absence of an external field. I will show evidence that this spontaneous vortex phase is caused by unconventional magnetism in the normal state.

Current flow map



$LaAlO_3/SrTiO_3$

Magnetic landscape



4Hb-TaS_2

Steric hindrance of NH_3 diffusion on Pt(111) by co-adsorbed O-atoms

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Unlike in enzymatic catalysis, industrial catalysts typically operate at elevated temperatures enhancing the influence of desorption, and there are no lock-and-key properties that bring the reactants to the active site. Instead, surface diffusion accomplishes this function; thus, a reactant's ability to diffuse on the catalyst surface to the active site while competing against thermal desorption may determine the catalyst's activity. This points out the importance of accurate determination of thermal diffusion coefficients and desorption rate constants under realistic reaction conditions on catalytic surfaces. Here we focus on the Ostwald process - a critically important stepping-stone for industrial production of artificial fertilizers, converting ammonia (NH_3) to nitric acid (HNO_3) in the presence of oxygen and water. The key to its success is the efficient oxidation of NH_3 to nitric oxide (NO) on a Pt catalyst.

We report a detailed Velocity Resolved Kinetics study of NH_3 thermal desorption rates from $p(2 \times 2)$ O/Pt(111). We find a large reduction in the NH_3 desorption rate due to adsorption of O-atoms on Pt(111). A physical model describing the interactions between adsorbed NH_3 and O-atoms explains these observations. By fitting the model to the derived desorption rate constants, we find an NH_3 stabilization on $p(2 \times 2)$ O/Pt(111) [1] of $0.147^{+0.023}_{-0.014}$ eV compared to Pt(111) [2] and a rotational barrier of $0.084^{+0.049}_{-0.022}$ eV, which is not present on Pt(111). The model also quantitatively predicts the steric hindrance of NH_3 diffusion on Pt(111) due to co-adsorbed O-atoms. The derived diffusion barrier of NH_3 on $p(2 \times 2)$ O/Pt(111) is $1.10^{+0.22}_{-0.13}$ eV, which is $0.39^{+0.22}_{-0.14}$ eV higher than on pristine Pt(111). We find that PBE and RPBE exchange-correlation functionals are unable to reproduce the experimentally observed NH_3-O adsorbate-adsorbate interactions and NH_3 binding energies at Pt(111) and $p(2 \times 2)$ O/Pt(111), which indicates the importance of dispersion interactions for both systems.

References

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[2] D. Borodin, I. Rahinov, O.Galparsoro, J. Fingerhut, M. Schwarzer, K. Golibrzuch, G. Skoulatakis, D.J. Auerbach, A. Kandratsenka, D. Schwarzer, T.N. Kitsopoulos and A.M. Wodtke "Kinetics of NH_3 Desorption and Diffusion on Pt: Implications for the Ostwald Process". ***Journal of the American Chemical Society (JACS*), 143, 43**, 18305–18316, **2021**

On the interaction of hydrogen with ceria in ambient conditions: hydride formation VS hydroxylation of the surface

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Ceria catalysts present a great potential for the selective hydrogenation of alkynes to alkenes and the hydrogenation of CO_2 to methanol [1]. Recent works suggest that the type of surface and subsurface hydrogen may play an important role, affecting both the activity and the selectivity in hydrogenation reactions. Interaction with hydrogen go typically through two routes: homolytic dissociation to form two hydroxyls and heterolytic route to form hydride and a proton, although other pathways are possible The hydrides are stabilized by oxidizing the cerium atoms next to the oxygen vacancies [2,3].

Using simultaneous X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy, and grazing incidence resonant X-ray scattering (GIXS) measurements at ambient conditions, we aim to understand both the structural and chemical changes occurring during reduction, oxidation, and interaction with hydrogen. We measured resonant X-ray scattering at Ce M_5 edge to distinguish between Ce^{4+} or Ce^{3+} species revealing dramatic changes in shape of the form factor. X-ray photoelectron spectroscopy shows that the surface was most oxidized when annealed in the H_2 atmosphere, suggesting formation of hydrides. Ceria can expand through the process, and this volumetric change can be observed in diffraction measurements. Correlation of all the simultaneously acquired spectral and diffraction data gains novel insights of the ceria-H_2 system.

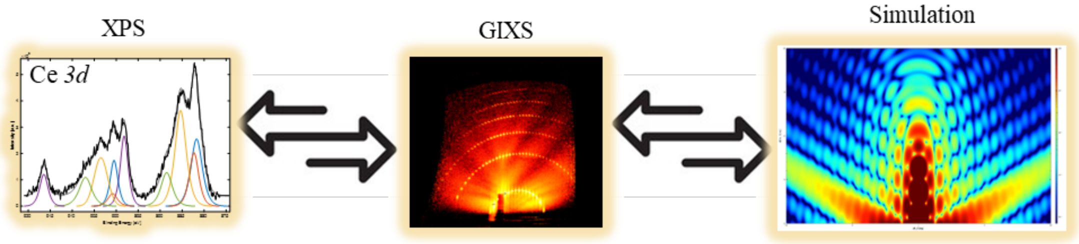

Fig. 1: *Schematic representation of the experiment process combining chemical information from XPS, structural information from GIXS and simulation of GIXS images with XPS as an input.*

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Analyzing and modeling of microrheological and adhesive properties of soft hydrated surfaces by AFM and flow cell tests.

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Hydrophilic, swellable surfaces, such as hydrogel coatings based on polyethylene glycol (PEG) or zwitterionic polymers, are known for their inertness when interacting with organic and inorganic matter. Apart from low adhesion, hydrogels can mimic living tissues owing to the mobility of the polymer network and presences of hydrophilic moieties, water and other components present on the cell surfaces. These outstanding properties imparting hydrogel coatings with resistance to attachment of and fouling by living cells, colloids, and biomolecules, which makes them widely used in many applications, from medical devices to membrane coatings. However, the physical mechanism of the cell and microparticle attachment in aqueous environment still leave many open questions, especially, regarding connection of microscopic and macroscopic adhesion kinetics.

To address this problem, we consider the most general case of adhesion of a solid particle with a soft water-swollen and viscoelastic gel under water, using polystyrene micron- sized particles and bacteria on PEG-based hydrogels as a model system. We analyze the adhesion in two distinct ways, macroscopically and microscopically. At the macroscopic level, we examine the particle deposition rates on the hydrogels in a parallel plate flow chamber (PPFC), evaluating their spatial variation along the chamber using a new deposition model that separates bulk transport from the attachment kinetics at the surface. We seek to understand how the latter, characterized by macroscopic attachment rate constant, analogous to rate of first-order heterogeneous reaction, is related to appropriate characteristics of the surfaces and kinetics at the microscopic single-particle level.

At the microscopic level, we examine attachment of a single particle on differently prepared and swollen hydrogels using AFM force spectroscopy (FS) with approach/retraction velocities and dwell time of attached particle before retraction as appropriate kinetic variables. The FS data show a nontrivial dynamic behavior, poorly described by the classical static adhesion models and pointing to the critical importance of relaxation phenomena in adhesion kinetics. To analyze FS data, we propose and successfully apply a new model that amends the classical models for two types of relaxation, osmotic and viscoelastic. This work is a step towards a unified picture of dynamic attachment, which connects microscopic and macroscopic kinetics, ultimately targeting to clarify the relation of both to physicochemical characteristics of the particle/cells and hydrogels.

Charge Transport across Biomolecular Electronic Junctions. Ultraviolet and X-ray Photoemission Spectroscopy Studies

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Biomolecules such as proteins and peptides are potential candidates for building diverse functional electronic devices. Measuring and controlling electron transport (*ETp*) through these molecules, especially, as assemblies on solid substrates, i.e., part of an electronic device structure with solid electrodes, is a major goal of bio-molecular electronics. The electronic structure of the peptide/protein monolayer and/or its orientation in contact with an electrode can be directly related to the energy barrier and electrode/molecule coupling in the resulting junction.

Ultraviolet and X-ray Photoelectron Spectroscopies (UPS, XPS) with their high surface sensitivity have been used extensively to study the electronic and chemical structure of *molecular* thin films or monolayers on solid surfaces. Here we show how UPS and XPS measurements can provide a crucial information for understanding the mechanism(s) of *ETp* through biomolecule/Au electrode-containing junctions.

In the first example we show how the spatial position of a singe tryptophan "dopant" in a linear oligo-alanine chain may significantly influence *ETp* across a self- assembled monolayer of these peptides between gold contacts.[1] In the second example we explore the effect of the side-chain of the peptide (*2Ala* vs *2Trp*) on its electronic properties.[2]

In the two next examples, the bacterial electron transfer protein Azurin (*Az*) [3] and a mutant (*N42C Az*)[4] are studied on Au substrates. We find that the *ETp* mechanism can be changed by changing just a linker (binding)[3] or the orientation[4] of the protein with respect to the Au substrate.

Finally, we demonstrate that the direction of current rectification and the conductance-voltage characteristics of the Photosystem 1 complex (*PS1*) can be controlled by its orientation on Au substrates.[5]

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