5th Molecular Simulations Workshop
Northeastern Regional Edition

Contents

NJIT
New Jersey Institute
of Technology

1 Invited Talks

1.1 Prof. Brandon Bukowski
Designing Solvent Microenvironments in Zeolite Catalysts using Atomistic Simulations for Sustainable Fuels and Chemicals

Johns Hopkins University

There is a critical societal need to develop new selective heterogeneous catalysts that enable large-scale decarbonization of the transportation and chemical industries. Catalytic valorization processes that utilize biomass derived from agricultural waste are typically selectivity-limited which limits their commercial viability. One exemplar catalyst family includes crystalline nanoporous solids such as zeolites which are employed in a wide range of chemical processes due in part to their tunable shape selectivity and framework-substituted cations. Reaction kinetics at internal zeolite acid sites can be modified by changing pore size, pore architecture, polarity, or acid site identity. These active site microenvironments impart shape-selectivity that preferentially stabilizes transition states and unique water matrices that in turn influence the stability of reactive intermediates. The large design space of zeolite catalysts including their pore architecture, polarity, and active site identity complicates comprehensive kinetic studies to predict new selective catalysts. Computational modeling of kinetic mechanisms in heterogeneous catalysis has emerged over the last few decades as a tool to predict both the structure and function of active sites to accelerate catalyst design. Here we will discuss how synergistic combinations of density functional theory (DFT), molecular dynamics, and machine learning techniques can provide design principles to design new selective zeolite catalysts for fuels and fine chemicals.

1.2 Prof. Mark Tuckerman
Synthesizing Machine Learning, Molecular Simulation, and Experimental Strategies for the Design and Analysis of a New Class of High-Performance Battery Electrolytes Exploiting the Grotthuss Structural Diffusion Mechanism

New York University

Candidate systems for next-generation electrolyte materials, such as deep eutectic solvents and ionic liquids, often suffer from high viscosities, which suppresses rates of charge transport and limits their performance characteristics. A strategy for circumventing this problem is to leverage the structural or Grotthuss mechanism of proton transport through hydrogen-bond networks, in which charge transport occurs through a series of proton hops from donor to acceptor. Liquids that support the Grotthuss mechanism can exhibit high proton diffusion rates even when rates of vehicular charge transport are poor. In this talk, I will describe a project aimed at leveraging machine learning and quantum simulation strategies, in combination with experimental synthesis and characterization to develop novel classes of battery electrolytes and fuel-cell membrane compositions based on the structural/Grotthuss diffusion mechanism. The workflow involves identification of a suitable proton-carrier liquid, a proton source, and a redox-active species capable of undergoing proton-coupled electron transfer (PCET) reactions. I will discuss the selection of candidate chemical species for each of the components, protocols for combining these components into a high-performance electrolyte, initial results, and next steps in the evolution of the project. I will show that the performance of candidate systems is strongly determined by nuclear quantum effects that operate on both local and extended length scales. This work will serve to illustrate both the power of modern computational approaches in the design of electrochemical systems but also to broaden the perspective on what constitutes a "breakthrough" electrolyte.

1.3   Prof. Rodrigo Freitas
Chemical Short-Range Order in Metallic Alloys

Massachusetts Institute of Technology

Metallic alloys often form phases - known as solid solutions - in which chemical elements are spread out on the same crystal lattice in an almost random manner. The tendency of certain chemical motifs to be more common than others is known as chemical short-range order (SRO) and it plays a prominent role in alloys with multiple elements present in similar concentrations due to their extreme configurational complexity (e.g., high-entropy alloys). Short-range order renders solid solutions "slightly less random than completely random", which is a physically intuitive picture, but not easily quantifiable due to the sheer number of possible chemical motifs and their subtle spatial distribution on the lattice. In this seminar I'll present an approach to predict and quantify the SRO state of an alloy with atomic resolution, incorporating machine learning techniques to bridge the gap between electronic-structure calculations and the characteristic length scales of SRO.

2 Posters

2.1 Andrei Kolesnikov, Explicit Water Model Solvation Pressure in Carbon Pores During Electrosorption

New Jersey Institute of Technology
Authors: Andrei Kolesnikov; Gennady Y. Gor

Nanoporous carbons play an important role in different electrochemical applications and, in particular, are widely used as porous electrodes in super-capacitors. Ions in aqueous electrolytes form the electrical double layer on the charged electrode-solution boundary, which can lead to a complex physical picture in nanosized pores. In this work, using molecular dynamic simulations, we studied the structure of the electrical double layer and the developed disjoining pressure in slit graphitic micropores immersed into a 1:1 aqueous electrolyte. We observed an oscillatory behavior of the force between two carbon surfaces, which originated from the layering of water molecules between them. The influence of surface charge density on the disjoining pressure was additionally quantified. We showed that the biggest effect is observed in the smallest pores, and it is gradually reduced with the pore width increase. Our results can be used in the further development of a theoretical framework for the description of electrosorption-induced deformation.

2.2 Andres Cifuentes-Lopez, Copper-induced Dimerization of Bacterial Chemoreceptors Controls Energy Taxis

Rutgers University-Newark
Authors: Andres Cifuentes-Lopez; Katherine Leon Hernandez; Natalia Nemeria; Colin Kinz-Thompson

Chemoreception is an important biological process that bacteria use to navigate their environment by responding to chemical cues, such as amino acids. In Escherichia coli, receptors known as methyl-accepting chemotaxis proteins (MCPs), like Tar and Tsr, detect and bind specific amino acids through their ligand-binding domains (LBDs). These MCPs are homodimeric receptors, and each MCP protomer in a dimer has its own LBD. Recently, using native mass spectrometry we experimentally observed that a single copper ion can bind to and stabilize two Tsr LBD protomers as a dimer. We hypothesized that this copper-induced oligomerization is crucial for Tsr's role in energy taxis, in which Tsr engages in chemoreception of the proton motive force (PMF) through a currently unknown mechanism. Here, we have used computational modeling and simulations to understand how copper can specifically bind to Tsr and regulate its chemosensory abilities during energy taxis. Metal3D and AlphaFold3 predictions of a metal binding site in the Tsr dimer suggest that a metal cation specifically interacts with histidine in the Tsr LBD dimerization interface. Quantum mechanical single-point calculations using density functional theory of the minimal dimerization system of a histidine-copper-histidine interaction suggest a covalent bonding interaction occurs for both Cu(I) and Cu(II) ions, but not for other physiologically relevant divalent cations. Subsequently, we performed classical molecular dynamics simulations of the Tsr LBD dimer in the presence of Cu(II), which resulted in the copper ion stabilizing the Tsr LBD dimerization interface. Finally, to understand how copper may affect Tsr's ability to sense the PMF during energy taxis, we are currently conducting quantum mechanics/molecular mechanics simulations of copper-induced Tsr dimerization as a function histidine protonation. Our initial findings suggest that histidine protonation modulates the dimerization interaction between Tsr protomers and Cu(II), and thus, may couple Tsr dimerization to the PMF—enabling Tsr to play a crucial role in energy taxis.

2.3 Ashley Guo, A Data- and Information-Driven Approach for Computational Soft Materials Design

Rutgers University–New Brunswick
Authors: Ashley Z. Guo

Controlling the emergence of order out of disorder is an overarching goal in the engineering of biological and soft materials. Conventional computational approaches have relied strongly on multi-scale molecular simulations aided by enhanced sampling techniques, including the recent proliferation of machine learning based methods. An exciting direction in the computational design of soft materials incorporates ideas from information theory into these approaches, drawing upon the connection between thermodynamic entropy and information entropy. This poster will highlight our recently-established research group's current interests at the intersection of molecular simulation, machine learning, and information theory, including new directions in developing polypeptide-based materials for

contaminant capture in wastewater, as well as characterization of polymer phase separation using data compression algorithms.

2.4 Augustine Onyema, Molecular Dynamics Simulations of the Structural Effects of Oncogenic Mutations in the Nucleosome

The Graduate Center, City University of New York
Authors: Augustine Onyema; Rutika Patel; Sharon Loverde

The information available to the cell to initiate, control, or stall metabolic processes is housed in the genome, whose monomeric unit is the nucleosome core particle (NCP). The nucleosome core particle (NCP), in conjunction with DNA-binding proteins like chromatin remodelers and transcription factors, forms the fundamental cellular apparatus essential for transcription, DNA repair, and DNA replication processes. These cellular processes are driven by the dynamics of the NCP, together with DNA binding proteins. However, oncogenic mutations within the histone core can disrupt chromatin remodeling mechanisms, including histone exchange and nucleosome sliding. Certain tumor cells biochemically exploit these dynamics to aid their proliferation in different cancer types, including glioblastoma, leukemia, lung carcinoma, and chondroblastoma. Mutations in the core histone proteins (H2B and/or H4) seen in uterine cancer have been shown to destabilize the H2B-H4 protein interface impact the stability of the histone octamer. Here, we ran 36 μs all-atomistic simulations of the wild type (WT), H2BE76K and H4R92T systems of the NCP using AMBER forcefields at different salt concentrations of 0.15 M and 2.4 M on Anton 2. The results showed a destabilization of the H2B-H4 interface in the mutant systems (H2BE76K and H4R92T). This destabilization was characterized by a decrease in the number and lifetimes of the hydrogen bonds between interacting amino acids in the H2B α_2 and H4 α_3 helices. We find that Mutation also shifts the dihedral angle between the planes of H2B α_2 and H4 α_3 helices. Free energy calculations indicated that, upon mutation, the H2B/H4 interface has a less favorable binding free energy. The WT was more stable than the mutant systems at all concentrations. The H2BE76K and the H4R92T mutations increased the interhelical distance between the H2B α_2 and H4 α_3 helices with the H2BE76K being the most destabilized. The undermined electrostatic interaction at the H2B-H4 interface decreased the dynamic cross correlation of the amino acids at that interface.

2.5 Daniel Mottern, Functionalized Covalent Organic Frameworks for PFAS Removal

New Jersey Institute of Technology
Authors: Daniel Mottern; Joshua Young

Perfluoroalkyl substances (PFAS) are a family of several thousand fluorinated chemicals that, due to their strong carbon-fluorine bonds, are resistant to degradation, and have accumulated over time in the environment. These chemicals have also been associated with health risks including cancer and birth defects. The danger of PFAS molecules, combined with the difficulty of remediating them with current techniques, has led to increased interest in discovering new remediation techniques. Nanoporous crystalline materials, such as metal- and covalent-organic frameworks (MOFs and COFs) have gained significant interest as adsorbent materials for the removal of PFAS and other aqueous contaminants. To accelerate the materials discovery and design process, we have focused on using Density Functional Theory (DFT) to study the interactions between pristine and functionalized COF structures with different PFAS molecules. In this work, we have focused on two ntirogen-based COFs, COF-300 and BFCOF-1, two functional groups (-CF3 and NH2 functional groups), and three PFAS molecules of varying chain lengths and head groups (PFOA, PFOS, and TFA). From our DFT simulations, we have found that the addition of CF3 and NH2 functional groups leads to stronger interaction with PFAS molecules than the pristine COFs. In addition, we found that deprotonated PFAS molecules show improved adsorption in our functionalized COF systems compared to neutral molecules.

2.6 Diana Marlen Castaneda Bagatella, Studying carbocation formation and rearrangements using metadynamics simulations

New Jersey Institute of Technology
Authors: Diana Marlen Castaneda Bagatella; Pier Alexandre Champagne

The carbocations and their rearrangements have significant importance in synthetic organic chemistry, the biosynthesis of terpenes, and petroleum chemistry. The formation of carbocations, often from neutral electrophiles undergoing ionization, can only be studied accurately with explicit solvation models, and as such, the activation-free

energies of such pathways have not been studied. To develop an approach to this problem, we first optimized our substrates of interest using density functional theory (DFT). Then, we performed ab initio molecular dynamics simulations (AIMD) and metadynamics simulations with explicit solvation. Such calculations allow the free energy surface of reactions to be reconstructed along well-defined collective variables, employing the known accuracy of DFT methods in organic chemistry. The results of these t-butyl chloride simulations will be combined with the investigation of machining potentials (MLPs) to sample all the possible configurations and pathways of those invisible intermediates at a lower computational cost, and similar simulations will be performed to prove that secondary carbocations do not exist as stable intermediates and study other carbocationic rearrangements.

2.7 Duwage Perera, Molecular Dynamics Simulation Study of PFAS Behavior in an Argon Nanobubble

New Jersey Institute of Technology
Authors: Duwage C. Perera; Jay N. Meegoda

Per- and polyfluoroalkyl substances (PFAS) are persistent environmental contaminants known for their complex interactions with various interfaces hence called, "Forever Chemicals" Understanding their behavior at the nanoscale is crucial for developing effective remediation strategies. In this study, we employ Molecular Dynamics (MD) simulations using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to investigate the behavior of PFAS molecules in an argon nanobubble, to investigate the potentials to use as a remediation technique. The simulations provide insights into the distribution, orientation, and interactions of PFAS at the gas-liquid interface, revealing their tendency to accumulate at the nanobubble surface. We explore the influence of PFAS concentration and bubble size on these interactions. We also plan to highlight key mechanisms driving PFAS aggregation and potential impacts on bubble stability. This study advances our understanding of PFAS behavior in nanoscale environments, offering valuable information for the development of nanoscale remediation techniques that we employ in our experiments.

2.8 Elizaveta Tremsina, Atomistic Study of Current-driven Dynamics of Magnetic Skyrmions

Massachusetts Institute of Technology
Authors: Elizaveta Tremsina; Geoffrey S.D. Beach

Magnetic skyrmions, two-dimensional quasiparticles formed by a local twist in the magnetization, are great candidates for use in novel spintronic devices, especially since they can be efficiently driven by spin torques through magnetic media. This, however, requires a thorough understanding of their dynamic stability, maximum velocity of propagation, as well as their dynamic deformations, which have been observed experimentally and in simulations, but not universally understood for skyrmions in all magnetic materials.
Here, the unique capabilities of fully atomistic magnetic modelling in the VAMPIRE software, in conjunction with the Thiele formalism, are used to perform an extensive study of skyrmions driven by spin orbit torque in materials with multiple magnetic sublattices. We systematically analyze the nature of structural deformations of the moving skyrmions which also limit their maximum velocity of propagation. Then, using the numerically simulated travelling skyrmion profiles, we calculate the localized effects of the gyrotropic, dissipation and driving forces at various points around the skyrmion perimeter to explain the deformation effects.

2.9 Geordy Jomon, An Efficient Molecular Dynamics Method for Calculating the Bulk Modulus of Confined Fluids

New Jersey Institute of Technology
Authors: Geordy Jomon; Jason Ogbebor; Santiago Flores Roman; Gennady Gor

Nanoporous materials have many applications in catalysis, separation processes, as adsorbents or desiccants, and more. It is important to understand the behavior of fluids present in these nanopores. Fluids present in these pores have different thermodynamic properties compared to bulk such as density, phase transition, diffusivity, and compressibility caused by the interaction between the solid pore walls and the confined fluid. These properties can be predicted using Monte Carlo (MC) and Molecular Dynamics (MD) methods. However, these methods can be inefficient and time consuming for large pores. A new method is proposed that can efficiently compute the compressibility of the confined fluid by using a well-established relation from statistical mechanics traditionally

applied to bulk fluids. This method offers improved computational efficiency, making it feasible to explore the effects of confinement on the compressibility across a broader range of pore sizes.

2.10 Gizem Celebi Torabfam, Salting-out Effect on Amyloid-like Fibril Elongation From Amphipathic Peptides

New Jersey Institute of Technology
Authors: Gizem Celebi Torabfam; Warin Rangubpit; Punyakanthi Sandeepani Thilakaratne; Cristiano L. Dias

Amyloid fibrils are a hallmark of somatic degeneration associated with aging, particularly implicated in the development of neurotoxicity and dementia through their role in the pathogenesis of Alzheimer's disease and other amyloidoses. The aggregation of amyloid-β fibrils into plaques is a complex process influenced by their interaction with the surrounding microenvironment, which poses significant challenges to therapeutic intervention. Ionic strength, specifically sodium and chloride ions essential for neuronal function, plays a pivotal role in modulating peptide self-assembly by affecting aggregation kinetics and molecular interactions. Despite advances in quantitative methodologies that elucidate the mechanisms of protein and peptide self-assembly, the precise regulation of these processes by microenvironmental factors remains insufficiently understood. In this study, we explore the specific impact of ionic strength on fibril elongation using a neutral fibril model composed of amphipathic (FKFE)2 peptides, avoiding the need for extensive simulations required for full-length amyloid-β peptides. Our results demonstrate that a 150 mM NaCl concentration maximizes the elongation rate of (FKFE)2 peptides. This effect is primarily driven by the salting-out phenomenon in solution and the surface-catalyzed secondary nucleation reactions occurring at an optimal rate. The accelerated fibril formation can be attributed to the reduction of electrostatic repulsion between the fibril tip surface and monomeric peptides, thereby facilitating more efficient assembly.

2.11 Hang Zhang, Hydrophobicity and Triboelectricity at Polymer Surface

Princeton University
Authors: Hang Zhang; Sankaran Sundaresan; Michael A. Webb

Surface is important for many properties of polymers, such as hydrophobicity, triboelectricity, etc. These properties lead to various applications such as anti-fouling coating and energy generation. Molecular dynamics simulation provides a powerful tool to gain atomic level insights into surface systems. By simulating soft polymer surface with water/ion droplet, our works show the molecular origin of polymer surface hydrophobicity and provide new evidence to the long-standing mystery of insulator triboelectricity.

2.12 Jason Ogbebor, Phase Stability of NiCr Alloy from Atomistic Simulations

Massachusetts Institute of Technology
Authors: Jason Ogbebor; Rodrigo Freitas

Complex concentrated alloys (CCAs), a class of materials in which three or more metallic elements are mixed in similar concentrations, exhibit exceptional combinations of mechanical properties and have been shown to avoid common limitations of traditional alloys. The compositional space available for CCA design is substantially larger than that of traditional dilute alloys, which has sparked considerable interest in the materials community. But in practice, equilibrium thermodynamic constraints, materials selection considerations, and post-synthesis thermo-mechanical treatments render this space too complex to be navigated effectively through trial-and-error or empirical guidelines. These constraints motivate the development of high physical-fidelity tools to probe thermodynamic stability and navigate the complexities of the compositional design space, including predictive methods of calculating equilibrium phase diagrams. This work aims to combine a machine-learning interatomic potential with state-of-the-art simulation techniques to efficiently model phase stability in a binary alloy system as a proof of concept towards predictive modeling of phase stability in CCAs.

2.13 Liza Basharova, Viscosity of Binary Solutions of Organophosphates: Molecular Dynamics Predictions

New Jersey Institute of Technology
Authors: Ella V. Ivanova; Elizaveta Basharova; Gennady Y. Gor

Understanding the behavior of organophosphates in case of leakage or destruction is an important task especially when they mix with water or other contaminates. To do so we have calculated viscosity of DMMP (dimethyl-methylphosphonate) binary mixture with water and methanol. We used MD software (LAMMPS), i.e. Green-Kubo method for our simulations. Though this method is time consuming it gives fair results. DMMP-Water mixture shows maximum on the plot, so we have examined such behavior and concluded that hydrogen bonding is responsible. To be sure we did some quantum-mechanical calculations to see the shift of the specific bond in IR-spectra depending on the number of water molecules around DMMP molecule. Calculated spectrum was compared with experimental one and qualitatively they coincide. We saw a shift in $P = O$ bond and we concluded that DMMP forms hydrogen bonds with water and can explain the peak in viscosity.

2.14 Mingze Zheng, Unveiling Structural Insights of RE/Beta Zeolites for Selective Biomass Valorization

Johns Hopkins University
Authors: Mingze Zheng; Shivangi Borate; James W. Harris; Brandon C. Bukowski

Rare-earth (RE) metal-incorporated zeolite Beta presents a promising strategy for improving conversion and selectivity specifically in the ethanol-to-olefins (ETO) process for sustainable aviation fuel (SAF) synthesis,1 while also offering potential applications in other catalytic reactions such as isomerization, hydrogenation, and alkylation.2–4 This study provides a comprehensive structural characterization of RE acid sites in zeolite Beta, combining advanced density functional theory (DFT) simulations with experimental spectroscopic and kinetic techniques. Our investigation begins with yttrium site configurations formed through post-synthetic heteroatom incorporation within the zeolite Beta framework, analyzing their physical properties - such as Y-O coordination numbers, Y-O bond lengths, and adsorbed pyridine IR spectra - which we then correlated with experimental data. We propose five distinct yttrium site structures at intersection T sites in zeolite Beta from a set of over 60 plausible configurations. These configurations were further refined based on their stability and consistency with experimental observations to yield a set of experimentally accessible Y site configurations.

These structural insights were then applied to key reactions in the Meerwein-Ponndorf-Verley (MPV) reaction and ETO process, including ethanol dehydration and aldol condensation, within RE-incorporated zeolite Beta using our previously identified site configurations. Additionally, we are currently exploring RE/Beta deactivation and regeneration during the ETO process, guided by our understanding of active site structures. Our findings not only provide atomistic insights into acid site requirements and kinetics of RE/Beta, but also set the stage for their application in a wider range of sustainable catalytic processes. This work demonstrates how designing active site structures can reduce deactivation in next-generation SAF synthesis catalysts, and further contributes to the broader objectives of reducing aviation-related CO2 emissions and advancing sustainable energy solutions.

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2.15 Nicholas Corrente, Modeling Adsorption of Simple Fluids and Alkanes on 3D Nanoporous Carbons

Rutgers University
Authors: Nicholas J. Corrente; Elizabeth L. Hinks; Aastha Kasera; Raleigh Gough; Peter I. Ravikovitch; Alexander V. Neimark

Predicting adsorption on nanoporous carbonaceous materials is important for developing various adsorption and membrane separations, as well as for oil and gas recovery from shale reservoirs. Here, we explore the capabilities

of 3D molecular models of disordered carbon structures to reproduce the morphological and adsorption features of practical adsorbents. Using grand canonical Monte Carlo simulations, we construct a series of adsorption isotherms of simple fluids (N_2, Ar, CO_2, and SO_2) and a series of alkanes from methane to hexane on two model 3D structures, purely microporous structure A and micro-mesoporous structure B. We show that structure A reproduces the morphological properties of commercial Norit R1 Extra activated carbon and demonstrates outstanding agreement between the simulated and experimental adsorption isotherms reported in the literature for all adsorbates considered. This work provides a new insight into the specifics of structural and adsorption properties of nanoporous carbons and demonstrates the advantages of using 3D molecular models for predicting adsorption hydrocarbons and other chemicals by MC simulations.

2.16 Pranav Roy, Ab-initio Design of Mild Temperature Ammonia Synthesis Catalysts using Metal Nitrides

Johns Hopkins University
Authors: Pranav Roy; Brandon Bukowski

Ammonia production is a pivotal industrial process with global significance. The potential for catalysts to produce significant ammonia yields at reduced temperatures and pressures could transform modern ammonia production, particularly in hydrogen storage and transportation. Metal nitrides, due to their ability to furnish surface nitrogen atoms for ammonia production, emerge as promising candidates in this pursuit. In this work, we employed periodic Density Functional Theory (DFT) to investigate the associative Mars-van Krevelen mechanism, involving sequential hydrogenation of adsorbed nitrogen on binary nitrides, leading to ammonia desorption. We opted for this mechanism over the dissociative pathway due to the energy-intensive nature of breaking the nitrogen-nitrogen bond, essential in the dissociative pathway. We also investigated the influence of a quasi-one-dimensional Ni nanowire supported on manganese nitride substrates, revealing a simplified ammonia formation mechanism. Through a detailed microkinetic model, we quantified reaction rates and orders on the nitride surfaces, validated against experimental data for accuracy. Ultimately, we evaluated different phases and surfaces of manganese nitrides, constructing a surface phase diagram to determine the most energetically favorable structure under reaction conditions of nitrogen and hydrogen thermodynamic reservoirs. This ab-initio thermodynamic analysis guides the establishment of temperature and pressure conditions crucial for our chemical looping approach with metal nitride catalysts. By facilitating dynamic replenishment of vacancies in metal nitrides through phase transitions, this method enhances ammonia yields and offers catalyst regeneration potential.
Our research delves into the surface and reaction chemistry of metal nitrides, laying the groundwork for catalysts to produce higher ammonia yields under mild temperature and pressure conditions.

2.17 Shahid Akbar, Exploring Magnetic Bi-stability in Fe(II) Hofmann-type 2D coordination polymers

New Jersey Institute of Technology
Authors: Shahid Akbar; Farnaz Shakib

Magnetic bi-stability in Fe(II) Hofmann-type conjugated coordination polymers (CCPs) offers a pathway to innovative applications in data storage and molecular switching. In this study, we employ periodic Density Functional Theory (DFT) calculations with the PBE-D3+U functional to explore the effect of spin transition on the structural, thermodynamic, electronic, and magnetic properties of 2D Fe(II) CCPs focusing on a unit cell comprised of four hexacoordinated Fe complexes. Benchmarking of Hubbard U-correction values to determine the optimal parameter that aligns closely with experimental observations reveals the importance of this additional functional as PBE-D3 by itself wrongly assigns the low-spin (LS) state as the most stable phase of the material. A systematic spin transition study starting from the most thermodynamically stable CCP with four high-spin complexes (4HS) towards the 4LS one reveals the 2HS/2LS system as a meta-stable intermediate while the 1HS/3LS and 3HS/1LS are high energy-barrier transition states. This process is accompanied by a shrinking of the volume of the unit cell which we attribute to the shortening of Fe-N bond length from 4HS to 4LS. The outcomes of this research contribute to a deeper understanding of the mechanism of spin transition behavior in CCPs and lay the groundwork for the rational design of materials with tailored magnetic properties for advanced technological applications.

2.18 Siwaporn Sungted, Effect of Polar/Non-Polar Sequence Pattern on Peptide Aggregation in Hydrophobic and Hydrophilic Solvents

Kasetsart University
Authors: Siwaporn Sungted; Warin Rangubpit; Cristiano Dias; Jirasak Wong-ekkabut

The aggregation of amphipathic peptides into amyloid-like fibrils is related to several neurodegenerative disorders, including Alzheimer's and Parkinson's diseases. These peptides have been shown to interact with neuronal lipid membranes causing damage that leads to ion permeation. Here, we investigate effects of the polar/non-polar sequence pattern on peptide aggregation in different solvent conditions. We study peptides that are made from the same amino acids (4 Phe (F), 2 Lys (K), and 2 Glu (E)) distributed at different positions along the sequence. This includes a peptide where polar/non-polar amino acids alternate strictly along the sequence (i.e., FKFEFKFE), and peptides where non-polar and charged residues are segregated to N- and C- terminals, respectively, (i.e., sequences FFFKFEKE and FFFFKKEE).

Peptide aggregation was studied using molecular dynamics simulations in solvents differing in their degree of hydrophobicity, i.e., octane and water. In addition, mixtures of these solvents were also explored. Atomistic simulations show that all these peptides aggregate adopting mostly random coil conformations except for the FKFEFKFE peptide, which preferentially forms β-sheets in pure water. In this environment, hydrophobic interactions primarily cause the formation of a globular cluster, while in octane, electrostatic interactions between charged residues lead to a cylindrical cluster. Both the environment and peptide sequence influence the formation and placement of hydrogen bonds, as well as which parts of the peptide participate in these interactions. In water-octane systems, peptides localize at the polar/non-polar interface consistent with our calculated free energy which is the lowest at this interface. The percentage of β-sheets increase significantly for the FKFEFKFE peptide. The aggregation behavior of the FFKKFFEE peptide was examined, revealing that it segregates non-polar and polar residues on different faces when adopting an α-helix. Furthermore, we find that two peptides require more energy to form β-sheets at the water-octane interface compared to their formation in the bulk solvent. Findings from this study provide valuable insights into the interplay between peptide properties and solvent environments.

2.19 Vailankanni Rodrigues, Investigating the RNA Recognition Motifs of the disease-associated PTB1 through molecular simulations

Rutgers University - New Brunswick
Authors: Vailankanni L. Rodrigues; Gregory L. Dignon

Polypyrimidine tract binding protein 1 (PTB1), a subset of the hnRNP family and part of the PTBP1 gene , has been under or over-expressed in cancer and autoimmune diseases like Multiple Sclerosis or Lupus. With its four RNA recognition motifs, this versatile protein demonstrates its potential in pre-mRNA splicing, polyadenylation, and other processes. Here, we run all-atom simulations using Replica Exchange Molecular Dynamics and Well-Tempered Metadynamics to explore its protein-RNA interactions and examine the pathogenesis of this disease-related RNA-binding protein. This knowledge can help us better understand their usage in biotherapeutics or drug design.

2.20 Vaishnavi Shesham, Extracting the Information about Protein Dynamics and Function Contained within a Protein Language Model using Molecular Dynamics Simulations

Rutgers University – Newark
Authors: Vaishnavi Shesham; Andres Cifuentes-Lopez; Karl Gaiser; Brigitte Valladares; Jordania Urquizo; Colin Kinz-Thompson

The primary structure of a protein theoretically contains all of the chemical information required to determine its three-dimensional structure and biochemical function. Recently, machine learning-based language models called protein language models (PLMs) have been developed, which encode the "grammar" of these protein primary structures. PLMs are so powerful that they have successfully been used to predict the three-dimensional structure and the gene ontology keywords that describe a protein's function. The success of PLMs suggests that they contain information about the evolutionary history and functional principles governing proteins, however, it is unclear exactly what information they contain and how it can be extracted. Here, we have used a PLM called Evolutionary Scale Modeling 2 (ESM2) to optimize protein primary structures one amino acid at a time, and then measured the dynamics and function of those stepwise-optimized proteins to interpret how ESM2 assess which substitutions

make a protein "better." Using this approach, we optimized two fluorescent proteins (mRuby3, mClover3) and two antibiotic resistance proteins (beta-lactamase, kanamycin kinase) while varying the PLM size to analyze the different in silico directed-evolutionary paths that are taken. Molecular dynamics (MD) simulations were then performed to investigate how the conformational dynamics of the optimization intermediates change along those paths. Comparison of the root mean square fluctuations, and fraction of native contacts trajectories from those simulations has provided insight into the information that ESM2 contains about the principles that govern protein dynamics and function.

2.21 Warin Rangubpit, Comparative Analysis of CHARMM, LIPID21, and SLIPID Force Fields to study membrane damage by amyloid-like peptides

New Jersey Institute of Technology
Authors: Warin Rangubpit; Jirasak Wong-Ekkabut; Cristiano L. Dias

One of the mechanisms accounting for the toxicity of amyloid peptides in diseases like Alzheimer's and Parkinson's is the formation of pores on the plasma membrane of neurons. Recently, we have shown for the first time that unbiased all-atom simulations can be used to study this phenomenon for model peptides, and we studied effects of the polar-nonpolar sequence pattern on pore formation. Here, we focus on the effects of force fields on peptide adsorption, aggregation, and pore formation on lipid bilayers. To this effect, extensive simulations are performed using three popular force fields namely CHARMM36m, LIPID21 (L21), and SLIPID (SLIP). In these simulations, we use a negative membrane made using POPC:POPG lipids and a peptide made by alternating nonpolar (F) and polar (K or E) amino acids, i.e., (FKFE)2. The latter was shown to aggregate into fibril-like structures in solution like the configurations formed by amyloid peptides, which are heavily populated with β-sheets.
Our preliminary results show that the choice of force field should be a primary concern when starting simulations. Pore formation only takes place in our simulations when the CHARMM36m force field. In the L21 force field, peptides are biased towards aggregating in solution before becoming adsorbed onto the membrane. Surprisingly, peptides tend to form α-helices at the water-lipid interface in the SLIP force field, which inhibits them from aggregating into β-sheets.

2.22 Xiang Zhou, Data-Driven Design and Identification of Active Site Motifs in Amorphous Porous Polymer Catalysts using Molecular Simulation and Deep Reinforcement Learning

Johns Hopkins University
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Amorphous porous organic polymers (POPs) offer significant design versatility for specific catalytic applications due to their flexible and shape-selective nanopore environments. In particular, POPs functionalized with acid sites can catalyze esterification reactions and selective organic conversions, including the formation of cyclic ester carbonates from CO_2. The intricate and amorphous nature of POPs, however, complicates POP's computational catalysis workflow, resulting in challenges for feature engineering and high computational costs for high-throughput screening. We introduce a strategy comprising two cooperative methodologies to address these limitations. The first part of our strategy is applying a deep reinforcement learning (DRL) algorithm to streamline the discovery and optimization of potential catalysts within POP networks. Our approach leverages DRL to efficiently navigate the design of POPs to generate polymers with desired catalytic properties. The second part of our strategy uses image recognition and clustering tools to identify amorphous active site motifs based on their local environments generate surrogate models that are tractable with Density Functional Theory (DFT). In a simulation environment using porous aromatic frameworks (PAFs) as example initial monomers at different mixing ratios, our model aligns its learning trajectory towards improving desired textural properties. Our DRL environment training results demonstrate the potential and capability to improve the adsorption properties of polymers and to target specific catalytic properties as training objectives.

2.23 Yanqi Huang, Ab initio and Molecular Dynamics Approaches to Predict Methane Dehydroaromatization Deactivation Pathways in Mo/ZSM-5

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Methane, the primary constituent of natural gas, is an abundant chemical feedstock but its strong C-H bonds impede valorization to higher value hydrocarbon fuels. Methane dehydroaromatization (MDA) provides one route for direct conversion of methane to liquid hydrocarbons. Zeolite catalysts are typically employed in this reaction due to their shape selectivity and hydrothermal stability, for example Mo/ZSM-5 where MoOxCy ion exchange sites are proposed to be active and the ZSM-5 scaffold leads to improved aromatic selectivity with high atom efficiency. Despite this catalyst being active for MDA, numerous challenges including deactivation due to coking are prevalent. To develop stable MDA catalysts, the mechanisms by which carbonaceous deposits form must be understood to prevent deactivation. In this work, we combined Density Functional Theory (DFT) and molecular dynamics to explore MDA kinetics and the formation of carbonaceous deposits to discover new catalyst formulations with reduced deactivation or facile regeneration. To predict reaction rates, we must obtain accurate predictions for rate constants based on Gibbs free energies sampled with DFT. At MDA reaction temperatures (> 1000 K) traditional harmonic oscillator approximations to calculate adsorbate entropy will not be applicable due to adsorbates gaining local translational and rotational degrees of freedom. We performed ab initio molecular dynamics (AIMD) simulations at 1000 K to confirm that anharmonic modes were present, and applied mode decomposition methods to calculate adsorbate entropies using classical partition function methods. We found that aromatics react to form hydrocarbon pool species with lower intrinsic activation barriers than reactant methane, providing evidence that at higher conversions, aromatic chain growth may become kinetically dominant. These substituted aromatics adsorb more strongly at active sites than methane, and may play a role in deactivation if they are unable to desorb.

2.24 Yuliang Shi, Transferable High-dimensional Committee Neural Network Potential Energy Surfaces for Electrically-Conductive Metal-Organic Frameworks

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Two-dimensional metal-organic frameworks (2D MOFs) are a new class of low-dimensional materials that offer electrical conductivity on top of other known properties of MOFs, including permanent porosity and exceptionally high surface area, promising unprecedented breakthroughs in producing high-performance and cost-effective batteries, semiconductors, and supercapacitors. However, traditional simulation methods, while accurate, are too expensive to cover such extensive systems, or they may be more affordable but fail to adequately capture quantum effects. In this context, neural network potentials (NNP), which combine accuracy and computational efficiency, emerge as a promising approach for advanced materials simulations. Here, we utilize the power of active learning and committee neural networks (CNN) to achieve a transferable model by integrating trajectories from various 2D MOF structures, using only a few hundred configurations. Our model exhibits robust performance across different classes of secondary building units from our 2D MOFs database. We anticipate that NNP-based approaches will become increasingly crucial in the field of materials simulation in the future.