SYMPOSIUM BM03

Multiscale Modeling of Soft Materials and Interfaces
November 26 - November 29, 2018

Symposium Organizers
Sanket A. Deshmukh, Virginia Tech
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* Invited Paper

SESSION BM03.01: Multiscale Modeling of Soft Materials and Interfaces I
Session Chairs: Sanket A. Deshmukh and Meenakshi Dutt
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Back Bay B

8:00 AM BM03.01.01
Effects of Molecules Organization on the Mechanical Properties of Wood <u>Kai Jin</u> and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Wood is a biological material with outstanding mechanical properties resulting from its hierarchical structure across different scales. While the cellular structure and the winding angle between the stiff cellulose fibrils and the wood cell axis have been reported to be key factors for its high stiffness and strength at light weight, the role of the molecular organization of its chemical components: cellulose, hemicellulose and lignin, is still to be fully understood. At the molecular scale, most of the hemicellulose molecules attach on the surface of the stiff crystalline cellulose fibrils, while lignin molecules fill the rest space. By applying a recently developed full atomistic model of the wood cell wall material, we studied how wood benefits from this intriguing molecular organization by intentionally varying the material distribution so that hemicellulose and lignin are randomly mixed or lignin molecules attach on the cellulose surface. It is found that better adhesion between the cellulose fibrils are achieved with the material distribution found in natural wood. Further detailed studies on individual molecules reveal that the hemicellulose show higher adhesion than lignin with cellulose and the three-dimensional structure of lignin originates its higher rigidity. Moreover, the covalent crosslinks between hemicellulose and lignin molecules enhance the load transferring between them. Therefore, the material distribution found in natural wood forms a pathway for load transferring that materials with stronger interactions are paired together. Our study reveals the molecular principles that wood adapts to achieve the outstanding mechanical properties at the macro-scale, which could shed light on the design of composite materials.

8:15 AM BM03.01.02
The Effect of Cargo Topology on Microcompartment Assembly <u>Farzaneh Mohajerani</u> and Michael Hagan; Brandeis University, Waltham, Massachusetts, United States.

Bacterial Microcompartments (BMC) are roughly icosahedral shells found in bacteria that sequester enzymes involved in certain metabolic processes. Experiments suggest that some BMCs assemble by a pathway in which the enzymatic cargo first undergoes phase separation, after which the shell assembles around the dense cargo droplet. Other types of BMCs assemble in a single step, with simultaneous cargo coalescence and shell assembly. Computational studies suggest that the strength of interactions between cargo particles are a key determinant of the assembly pathway. However, the physical origins of these interactions remain unclear; in particular, whether they result from direct attractions between enzymes or are mediated by scaffolding proteins.
In this presentation we describe coarse-grained computational and theoretical modeling to study the effect of cargo interactions and cargo topology on microcompartment assembly. We present results of dynamical simulations that compare shell assembly when cargo coalescence is driven by direct cargo-cargo attractions or scaffold-mediated attractions. We find that cargo properties can dramatically influence assembly pathways. Depending on conditions, the presence of cargo may increase or decrease shell size in comparison to the intrinsic protein curvature. This result may explain recent experiments on different BMC systems in which empty BMC shells were respectively smaller or larger than full shells. In comparison to direct cargo-cargo attractions, our simulations identify a richer set of assembly behaviors for scaffold-mediated cargo attractions, and suggest that there are experimentally distinguishable differences between the two classes of systems. Understanding factors that control encapsulation of cargo by self-assembling shells is the first step for reengineering BMCs to construct drug delivery vehicles or customizable nanoreactors that encapsulate a programmable set of enzymes.

8:30 AM BM03.01.03
Development of Coarse-Grained Polystyrene and Poly(acrylic acid) Models—From Monomers to Polymer <u>Yaxin An</u>, Karteek K. Bejagam and Sanket A. Deshmukh; Virginia Tech, Blacksburg, Virginia, United States.

The self-assembly process of polymers and peptide amphiphile usually involves large time (~microseconds) and length (~micrometers) scales. Modeling of such a process using all-atom (AA) classical molecular dynamics (MD) simulations is a challenge. Coarse-graining is a technique to overcome these challenges, in which a group of atoms is represented by a bead. In this work, the coarse-grained (CG) models of the monomer's analogues of polystyrene (PS), i.e. ethylbenzene, and that of poly(acrylic acid) (PAA), i.e. propionic acid, are developed firstly to reproduce their corresponding experimentally

measured properties at 300 K. A 2:1 mapping scheme is used to map a ethylbenzene molecule to be a C2E bead and three BZ beads, while a propionic acid molecule was represented by a C2E bead and a COOH bead. The C2E bead represents the ethyl group in ethylbenzene and propionic acid, and three BZ beads constitute the phenyl group, and the COOH bead represent the carboxylic acid group. The bonded interaction parameters are obtained by matching the bond length distributions with all AA mapped trajectories. The nonbonded parameters of the C2E and BZ beads were taken directly from our previously developed hydrocarbon and benzene models, while the nonbonded parameters of the COOH bead was optimized to reproduce the density (ρ), self-diffusion coefficient (D), enthalpy of vaporization (Hv), and surface tension (γ) of propionic acid at 300 K. The ρ, Hv, D, γ of CG ethylbenzene and propionic acid models were in good agreement with their corresponding experimental values. The free energies of hydration (ΔGhydr) of ethylbenzene and propionic acid are within 10% of their experimental values. Finally, CG PS and PAA polymer models with 30 monomer units were constructed. The conformation of these polymer chains in a CG water model was studied at 300 K by MD simulations. Results of these CG MD simulations were in good agreement with those of the AA simulations.

8:45 AM BM03.01.04
Understanding Polyethylene Cross Linking with Dicumyl Peroxide (DCP) via Large Scale Molecular Dynamics Simulations with ReaxFF Reactive Force Fields Dundar E. Yilmaz, Dooman Akbarian and Adri C. Duin; The Pennsylvania State University, State College, Pennsylvania, United States.

Polyethylene (PE) is one of the widely used commercial polymers. Cross linking improve many properties of PE such as high dielectric strength, mechanical strength, low water permeability.
Cross-linked PE (XLPE) has emerged as the insulator of choice for high-voltage direct current (HVDC) power transmission cables due to its favorable dielectric properties, low water permeability, structural integrity at high temperature and chemical resistance.
Dicumyl Peroxide (DCP) has been used as an accelerating agent in cross linking PE. We investigated cross linking mechanisms and mechanical and electrical properties of XLPE systems using large scale molecular dynamics simulations. We first started with a non-reactive force field to understand diffusion of DCP molecules into the PE matrix with and without the influence of external electric field. Second, we employed eReaxFF to investigate cross linking mechanisms. ReaxFF reactive force fields first developed for hydrocarbons and later ported to different systems such as ceramics, metals and their oxides and provided precise results for those systems. eReaxFF is an extension to ReaxFF in which electrons are treated explicitly in a pseudo classical manner. We adopted a previous ReaxFF reactive force field and developed eReaxFF reactive force field to capture DCP-PE interactions, and investigated reaction mechanisms of crosslinking of PE via DCP under the external electric field using large scale molecular dynamics simulations. We investigated the effects of different parameters such as temperature, density, pressure and the ratio of peroxides to polyethylene on the formation of byproducts, distribution of functional groups and cross-linking. Furthermore we investigatedmechanical (tensile strength, bulk modulus) and electrical properties (dielectric strength) of the cross linked PE.

9:00 AM BM03.01.05
Modeling the Influence of Emergent Interactions Between Nascent Oligomers on the Sequences of Step-Grown Copolymers Kateri H. DuBay and Zhongmin Zhang; University of Virginia, Charlottesville, Virginia, United States.

The sequences of synthetic copolymers are notoriously difficult to control, and numerous complex protocols have been developed to help us do so. However, we lack a comprehensive understanding of what governs the sequential incorporation of different monomers into a chain for even the simplest of copolymerizations. To learn more, we performed coarse-grained modeling of a linear, step-growth copolymerization between two monomers. Our results demonstrate that transient associations and emergent self-organization among the reacting monomers and nascent oligomers can exert considerable influence over the sequential arrangement of monomers in the resulting chains, even when reaction barriers between the different monomer pairs are held constant. The magnitude of the effect we observe for differing co-monomer attractions can be explained by an emergent phase separation among the nascent oligomers – a phase separation that is both initiated and limited by the copolymerization.

9:15 AM BM03.01.06
Computational and Experimental Studies of Peptide: Silica Interactions Victor V. Volkov and Carole C. Perry; Nottingham Trent Univ, Nottingham, United Kingdom.

Structural properties of bioinorganic composites are of contemporary research interest in fields such as drug delivery, bone repair and biomimetics. While being a key material in bio-engineering applications, silica may be either hazardous or biocompatible depending on parameters such as particle size, shape or surface properties. Effective simulation at the quantum level of large silica-based bio-composites is necessary to gain a deeper insight into the properties of such materials. How to bridge between structural extraction from large scale classical simulation to predictions by quantum chemistry for silica based structures is the focus of our contribution. In this presentation we present MD and DFT simulation data, complemented by experimentally derived vibrational and optical spectroscopic data for the study of (a) 2nm silica nanoparticles, (b) the possible effects of local fields next to such nanoparticles and (c) the interaction of silica with 7-mer peptides.

9:30 AM BM03.01.07
Predicting Viscoelasticity, Strength and Fracture for Ideal Reversible Polymer Networks German A. Parada and Xuanhe Zhao; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Ideal Reversible Polymer Networks have well-controlled network structures similar to ideal covalent networks but exhibit transient properties due to the presence of reversible crosslinks. We have developed a theory to describe the mechanical properties of these ideal reversible polymer networks under small shear deformation, and have predicted that the networks behave as a single Maxwell element of a spring and a dashpot in series, with the instantaneous shear modulus and relaxation time determined by the concentration of elastically-active chains and the dynamics of reversible crosslinks, respectively. Due to the use of short polymer chains, we expected no contributions from polymer chain entanglements or chain relaxation, as the Rouse relaxation time is much shorter than the reversible crosslinks' characteristic time. The theory also provided general methods to (i) independently control the instantaneous shear modulus and relaxation time of the networks, and to (ii) quantitatively measure kinetic parameters of the reversible crosslinks, including reaction rates and activation energies, from macroscopic viscoelastic measurements. The theory and methods were validated experimentally using a 4-Arm polyethylene glycol hydrogel system. We have also employed the theoretical and experimental system developed to characterize the fracture modalities and mechanical properties under large uniaxial deformation at varying loading rates.

9:45 AM BM03.01.08
Revisiting the Strong Stretching Theory for pH-Responsive Polyelectrolyte Brushes Harnoor S. Sachar and Siddhartha Das; Mechanical Engineering, University of Maryland, College Park, College Park, Maryland, United States.

Polyelectrolyte chains grafted to a substrate attain a brush like configuration above a critical grafting density. Polyelectrolyte brushes (PE) have gained

significant attention in the last few decades due to a myriad of applications like flow control, biosensing, current rectification, ion manipulation etc. We present a self-consistent model of backbone charged pH-responsive PE brushes using the Strong Stretching Theory (SST). State of the art theoretical model (we refer to it as model 1) for the pH-responsive PE brushes assume a Boltzmann distribution for hydrogen ions both inside and outside the PE layer. In other words, the effect of the coupling between the brush ionization and local hydrogen ion concentration is not considered. This is a major limitation of the existing theory that has been hitherto overlooked. We propose a new theory that self-consistently calculates the correct hydrogen ion distribution by accounting for the appropriate coupling between the brush ionization and local hydrogen ion concentration. We obtain a pair of coupled ordinary differential equations in electrostatic potential and hydrogen ion concentration that are solved numerically to obtain (a) the monomer profile, (b) the distribution of chain ends, (c) the electrostatic potential, and (d) the hydrogen ion distribution. Our results indicate a larger deviation from the results of model 1 at lower bulk salt concentrations and higher pH values. The self-consistent theory always predicts a smaller brush height in comparison to that predicted by model 1. In addition, we observe an enhanced biasness of the monomer concentration profile towards the base than the brush tip.

10:00 AM BREAK

10:30 AM *BM03.01.09
Multiscale Modeling of Polymer at Solid and Soft Interfaces Paola Carbone; The University of Manchester, Manchester, United Kingdom.

The prediction of the adsorption and dynamics properties of polymers at solid and soft interfaces is an important technological and biological problem. Solid interfaces are indeed present in all polymer composites (where particles are dispersed into a polymeric matrix with the aim of improving its mechanical and rheological properties) but also relevant for many applications such as for coating. Polymers adsorb also at liquid interfaces in many industrial processes, such as liquid/liquid extractions, solvent displacement methods, or emulsifications, and also when used for biological applications, such as drug nanocarriers, biocompatibilizers, or protective coatings.
In this talk we will present a set of multiscale approaches developed over the years to predict the adsorption properties of polymers at solid surfaces (specifically carbon black) and soft interfaces (liquid/liquid and lipid membrane).
The aim of the multiscale technique is to balance the need to retain important chemical details allowing long simulations and ultimately to identify design rules to predict the polymer/interface adhesion properties as a function of surface roughness and polymer composition.

M. Zaki, P. Carbone, Langmuir **2017,**33, 13284
T. Taddese, P. Carbone, J. Phys. Chem. B, **2017,** 121, 1601
T. Taddese, D. L. Cheung, P. Carbone, ACSMacro Lett., **2015,** 4, 1089
T. Taddese, P. Carbone, D. L. Cheung, Soft Matter, **2015,** 11, 81

11:00 AM BM03.01.10
Effect of Structural and Material Heterogeneity on Failure in Fibrous Materials Sai S. Deogekar, Mohammad R. Islam and Catalin Picu; Rensselaer Polytechnic Institute, Troy, New York, United States.

Fiber networks occur abundantly at all length scales in the biological and non-living worlds. Various applications of such fibrous materials require them to maintain their structural integrity. Hence, an accurate understanding of the factors affecting failure at system subscale is important. Since these materials are structurally stochastic, heterogeneity plays a major role in determining the dominant failure mechanism and affects strength and toughness of the material. In addition, most of these networks naturally occur as composites (e.g. in various types of tissue). Previously, we studied the effect of heterogeneity in the strength of the inter-fiber bonds on the overall network strength. In this work we study the effect of structural heterogeneity and network architecture, on the macroscopic strength and strain-at-failure. We observe that increasing the structural heterogeneity increases the strain-at-failure while the strength remains unaffected. Thus, we propose to use structural disorder of these materials to control their toughness. Further, we investigate the behavior of network-based composites formed by embedding spherical inclusions, rigid or deformable, in a fibrous network. A small fraction of inclusions strongly affects the network stiffness and alters drastically the microscopic deformation and failure mechanisms. This is due primarily to the confinement effect of inclusions on the deformation of the network.

11:15 AM BM03.01.11
Simulating Polymers with Reactive MD—Cross-Linking, Stress/Strain, Degradation, Solvation Adri van Duin[2], Nick Austin[1] and Fedor Goumans[1]; [1]Software for Chemistry & Materials (SCM), Amsterdam, Netherlands; [2]Department of Mechanical & Nuclear Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Reactive molecular dynamics techniques such as ReaxFF afford insight at the atomistic level for complex chemical processes as well as for material properties which involve chemical bond breaking and formation. We will discuss recent developments in the ADF-ReaxFF software in the context of polymers.
A new bond boost method enables the atomistic simulation of cross-linking processes such as epoxy resin hardening at reasonable time scales. The cross-linking densities from these simulations are in good agreement with experiments.
Stress/strain properties and yield points can be obtained with ReaxFF while straining the system, including the underlying atomistic processes. Similarly, degradation rates and mechanisms under extreme conditions can be simulated with ReaxFF.
Finally we will discuss how the information from reactive MD runs, in particular the dynamic charges, may be used to refine our COSMO-RS thermodynamic predictions for solubilities and related properties.

11:30 AM *BM03.01.12
Diffusioosmotic and Thermoosmotic Transport in Nanochannels Grafted with End-Charged Polyelectrolyte Brushes—Continuum Calculations and Molecular Dynamics Simulations Siddhartha Das, Raja Maheedhara, Parth Rakesh Desai, Haoyuan Jing and Harnoor S. Sachar; University of Maryland, College Park, Maryland, United States.

Liquid flows in nanochannels grafted with polyelectrolyte brushes have been invariably retarded owing to the significant drag force imparted by the PE brushes. In a recent study, we proposed a paradigm shift in this understanding – we showed that for nanochannels grafted with end-charged brushes (having a charge density of σ), the electroosmotic (EOS) transport got massively augmented as compared to the brush free nanochannels having a wall charge density of σ. We argued that the presence of the end-charged brushes localized the charge density of the induced electric double layer (EDL) and hence localized the EOS body force away from the nanochannel wall, thereby ensuring a massive manifestation of the EOS body force eventually enforcing a larger EOS transport. Here we report our first Molecular Dynamics (MD) simulations based verification of this phenomenon. Furthermore, we carry out continuum calculations for the diffusioosmotic (DOS) and thermoosmotic (TOS) transport in such end-charged PE-brush-grafted nanochannels in presence of an axial concentration and an axial temperature gradient respectively to establish that these transports too get enhanced due to the

corresponding enhancement in the induced EOS transport. Furthermore, MD simulations are carried out to validate the continuum findings.

1:30 PM BM03.02.01
Effect of Solvent on the Molecular Structure and Electrical Conductivity of DNA <u>Busra Demir</u>[1], Sumeyye Gokce[1], Hashem M. Mohammad[2], Sunil R. Patil[4], Yuanhui Li[3], Josh Hihath[3], M. P. Anantram[2] and Ersin Emre Oren[1]; [1]Department of Biomedical Engineering, TOBB University of Economics and Technology, Ankara, Turkey; [2]Department of Electrical Engineering, University of Washington, Seattle, Washington, United States; [3]Electrical and Computer Engineering Department, University of California Davis, Davis, California, United States; [4]Department of Physics, College of Engineering Pune (COEP), Pune, India.

DNA is a promising molecule for molecular electronics due to its unique electronic and self-assembly properties. Understanding the nature of electrical conductance of DNA is essential for rational design and engineering of these soft materials for use in molecular electronics. The structure of double-stranded DNA (dsDNA) is known to be sensitive to solvent conditions and thus its electrical conductivity. Here, we first used Molecular Dynamics (MD) simulations to determine both the transformation path and the stable molecular conformations of DNA (CCCGCGCCC and TTTATATTT) in various solvent (water-ethanol mixtures) conditions. The MD trajectories revealed that there is a specific ethanol concentration, below which the B form DNA is stable. Above this threshold value, which also depends on the sequence, we observed that A form DNA is the stable form. These observations also validated by the circular dichroism experiments for the same DNA sequences. The MD simulations also revealed that for extremely high ethanol concentrations the DNA helix is destabilized and collapsed. We then selected representative structures along the transformation path using structural clustering algorithms, and calculate the wave functions near the HOMO-LUMO gap using Density Functional Theory (DFT). Finally, we used Green's functions based transport modelling to analyze conductivity of DNA. Our calculations reveal that the solvent conditions is an important factor that determines the device characteristics because it can significantly change the conformation and conductance of the DNA.

1:45 PM BM03.02.02
Determining the Binding Mechanisms of All 20 Natural Amino Acids to (hkl) Facets of Hydroxyapatite as a Function of pH <u>Sam Hoff</u>, Juan Liu and Hendrik Heinz; University of Colorado Boulder, Boulder, Colorado, United States.

Mineralization of hydroxyapatite is a complex and highly controlled process involving interactions of biological and mineral components. Understanding the basic interactions between individual amino acids and hydroxyapatite at the (001) and (020) surfaces at pH 7 and 5 is a crucial step in understanding the mineralization process and potentially aiding in designing peptides to direct and control growth of bone allograft and biomimetic materials. In our study, a combination of steered and unrestrained molecular dynamics simulations using the CHARMM36 and Interface force field parameters are used to study the dynamic nature of hydroxyapatite as well as the binding conformations of N and C capped amino acids. The results indicate that charged amino acids have a distinctly higher affinity to the mineral surface than non-charged amino acids. Binding site preferences, conformations, and the effects of pH and surface facet on the affinities are reported, and significant differences for Arginine, Glutamic Acid, Aspartic Acid, and Lysine quantified. The trends provide valuable insight into the affinity and binding mechanism of the building blocks of larger biological structures such peptides and proteins onto hydroxyapatite surfaces. The results will be useful in designing peptides to target specific bone facets for growth or suppression as well as potentially offering the ability to target specific bone sites where infections exist.

2:00 PM BM03.02.03
Elucidation of the Induced Chirality of Dansylglycine by Its Interaction with Human Serum Albumin <u>Aguinaldo R. Souza</u>[1], Izabelle Amorin Ferreira Boza[1], Valdecir F. Ximenes[1], Maurício I. Yoguim[1], Nelson Morgon[2] and Ignez Caracelli[3]; [1]Chemistry, Sao Paulo State University - UNESP, Bauru, Brazil; [2]Chemistry, Campinas State University, Campinas, Brazil; [3]Physics, Federal University at São Carlos, São Carlos, Brazil.

Human serum albumin (HSA) plays an important role in the transport of substances with pharmacological properties due to their high plasma concentration and specificity, placing it as the fundamental protein responsible for the pharmacokinetic implication of the drugs. The dansylglycine amino acid derivative (DG) is a fluorescent marker specific for the II site on the HSA. In addition, when binding to the protein, DG acquires chirality, a feature that can also be used to characterize the binding site of new compounds in albumin. This work aimed to elucidate the induction of chirality in the DG by its bonding to the HSA. Experimental Electronic Circular Dichroism (ECD) spectra of DG (100 μM) in the absence or presence of HSA (30 μM) in 50 mM sodium phosphate buffer pH 7.0 were obtained in a Jasco J-815 spectropololarimeter at 25 º C. The spectra were obtained with a resolution of 1 nm and a scanning speed of 50 nm/min. The theoretical ECDs were simulated using the Density Functional Theory (DFT) approach with the hybrid functional B3LYP and CAM-B3LYP in the base set 6-311 ++ G (2d, p) and the implicit Solvation Model based on Density (SMD) for the solvents ethanol, methanol, acetonitrile, water and tetrahydrofuran; the calculations were performed with the Gaussian09 program. The DG-HSA complex formation in buffer resulted in the appearance of a positive ECD spectrum centered at 346 nm. Considering that the ICD signal should arise from a chiral conformation of the DG acquired by binding in the protein, calculations were initially performed to obtain the stable conformations focusing on the inversion of configuration centered on the nitrogen atom: alpha-amino group. However, both configurations: R and S showed similar and positive ECD signals. Calculations of the potential energy surface (PES) of the DG were performed, focusing on the dihedral angles formed by the bonding of the -N(CH$_3$)$_2$ group of the naphthalene ring. The analysis of the various conformations obtained and their respective theoretical ECDs revealed that the 150 ° dihedral (ECD positive centered at 320 nm) presented excellent similarity with the experimental spectrum. On the other hand, the 80° dihedral showed a signal of the ECD spectrum opposite to that observed experimentally. In addition, we observed that the nitrogen atom of the -N(CH$_3$)$_2$ group presented the greatest contribution to the HOMO-LUMO transition that gives rise to the n-pi * electronic transition involved in the generation of the ECD signal. The molecular docking analysis, using the GOLD 5.5 program, of the complexation between DG and HSA revealed a conformation with a dihedral similar (150 °) to that obtained theoretically (DFT) and whose ECD is in agreement with the experimental result. In conclusion, through the study of the possible conformations for dansylglycine and the calculation of its theoretical ECD, it was possible to identify the origin of the ECD signal obtained by the complexation between DG and HSA.

2:15 PM *BM03.02.04
Understanding Malaria Pathogenesis Through Coarse-Grained Computational Modeling <u>Sulin Zhang</u>[1], Yao Zhang[3], Leann Tilley[4], Ju Li[2] and Subra Suresh[5]; [1]The Pennsylvania State University, University Park, Pennsylvania, United States; [2]Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; [3]Northwestern University, Evanston, Illinois, United States; [4]The University of Melbourne, Melbourne, Victoria,

Australia; [5]Nanyang Technological University, Singapore, Singapore.

A normal human red blood cell (RBC) is characterized by two distinct features: high deformability and discocyte shape, which underlie its biological functions, demonstrated by the repeated transit of RBCs (diameter ~8 mm) through narrow capillaries and and 1-2 mm interendothelial slits in the spleen. These two distinct features of RBCs can be comprised genetically or in a variety of pathological conditions, leading to severe RBC diseases. Here we present a coarse-grained RBC membrane model integrating an one-agent-thick lipid bilayer model and a string-of-bead spectrin network model to simulate the change of deformability of the infected RBCs by the malaria parasites (plasmodium falciparum). In particular, we show how malaria parasites harness several materials principles simultaneously to render the RBC losing its deformability during asexual stage (disease-causing stage) and how the parasites alter the entropy of the spetrin network to enable the RBC regain the deformability during the sexual stage (disease-transmission stage). Our simulation results suggest potential targets for the development of new antimalarial therapies

2:45 PM BREAK

3:15 PM *BM03.02.06
Structure and Dynamics of Polymers in Ionic Liquids Arun Yethiraj; University of Wisconsin, Madison, Wisconsin, United States.

Ionic liquids have generated considerable excitement for their varied potential applications and their interesting physical properties. The viability of ionic liquids (ILs) in materials applications is limited by their lack of mechanical integrity, which may be provided by mixing them with a polymeric material. Recent experiments on polymers in ILs have unearthed a wealth of interesting phenomena that raise fundamental questions. This talk focuses on computational studies of PEO in imidazolium ILs. We develop a physically motivated first principles force field for PEO and [BMIM] [BF$_4$]; this force field is in quantitative agreement with experiment with no adjustable parameters. Based on the same quantum calculations we develop a hierarchy of united atom models with decreasing resolution and increasing computational efficiency. Microsecond simulations are required to obtain converged properties of the polymer, which displays a combination of ring-like and extended conformations. The simulations show the existence of a lower critical solution temperature which arises from conformational restrictions on the polymer molecules at low temperatures.

3:45 PM BM03.02.07
Behavior of Polyethylene Glycol in Bulk and in Water as Studied by Multi-Scale Simulations Gokhan Kacar; Genetics and Bioengineering, Trakya University, Edirne, Turkey.

Polyethylene glycol (PEG) is an important polymer that has an enormous area of application especially in biomedical field such as drug carrier agent, hydrogel, and tissue engineering material. A thorough understanding of the molecular structure of PEG at different environments is important to devise better routes to develop materials with desired purposes. Although, PEG has been a widely studied material its molecular structure in bulk and in aqueous environment has been poorly investigated. In this work, we strive to perform multi-scale molecular simulations in order to study the physical behavior and molecular structure of PEG in dry environment and interacting with water. We initially perform Dissipative Particle Dynamics (DPD) simulations to create the structure of PEG. Later, we perform reverse-mapping of the atomistic coordinates to perform atomistic molecular dynamics simulations in order to observe the chain configurations and material properties of PEG.

DPD simulations result in successful prediction of the negative volume excess of PEG upon mixing with water. Here, we use a recent extension of the DPD method, where the non-bonded potential of DPD is modified by a Morse potential term to mimic the intermolecular attraction. The parameterization of the Morse potential is done by a mapping of the mixing energies of different hydrogen bonding bead pairs and from radial distribution functions (RDF) for the energy and equilibrium hydrogen bond length terms, respectively. DPD simulations yield preferential attraction of some chemical groups to water as quantified by radial distribution functions. Moreover, PEG chain structure is observed to deviate significantly from a random coil structure as a result of the end-to-end distances and radius of gyration values. Moreover, DPD simulations reveal that water plays a significant role in increasing the flexibility of PEG chains. The helical structures of PEG chains are quantified and a significant helicity of PEG chains is noted with a higher fraction in wet environment.

The reverse-mapped coordinates of DPD simulations of bulk PEG structure are used in atomistic simulations to compute the material properties such as coefficient of thermal expansion, elastic modulus and Poisson's ratio. The computed coefficient of thermal expansion is in line with the experimental prediction. The computed values mainly reveal that PEG becomes more elastic and less compressible upon addition of water. In addition, the experimental aggregation of water in PEG is observed from MD simulations. In all, the multi-scale procedure predicts the structural and material properties of a widely used PEG in dry and wet environment. The procedure presented herein can be applied to similar materials to gain a molecular and macroscopic understanding of their properties.

4:00 PM *BM03.02.08
Machine Learning Methods to Design Next-Generation Gas Separation Membranes Sanat K. Kumar; Columbia University, New York, New York, United States.

Machine Learning (ML) has been used for quite some time in analyzing large sets of data in a variety of disciplines in order to make predictions on new data. Although gas permeability data has been collected for polymer membranes for decades, only hundreds of data points are available in the literature out of the thousands of possibilities. In order to address the intractability of running thousands of different gas permeability studies, we use ML to build a model on existing data and predict which untested polymers are most likely to achieve superior gas separation performance.

4:30 PM BM03.02.09
Using Gel Actuated Smart Capsules for Particle Capture Svetoslav Nikolov[1], Alberto Fernandez-Nieves[2] and Alexander Alexeev[1]; [1]Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; [2]School of Physics, Georgia Institute of Technology, Atlanta, Georgia, United States.

Advancements in nanotechnology over the last two decades have allowed researchers to tackle a number of critical biomedical problems on the microscale, like site-specific drug delivery and micro-sensing. Microdevices which can selectively capture nanoparticles at a given rate are particularly interesting as they are critical for the development of enzymatic bioreactors which are used in many in vivo micro-sensing applications. These devices could also be used for origin of life studies, where the ability to bring in particles at predefined rates can be used to carry out complex chemical reactions. In our work, using dissipative particle dynamics, we leverage the large volume changes of microgels to design a novel microdevice which can be used for nanoparticle capture. Our device is made up of a perforated rigid spherical shell that is embedded with a spherical microgel. Upon application of an external stimulus the gel swells, expanding through the perforated holes and making contact with the external nanoparticle rich solution. After removal of the external stimulus the microgel collapses into the shell interior, bringing along with it nanoparticles from the external solution. The area around each of the perforations is functionalized with a polymer brush which is used to achieve chemical gating, when the gel is in the collapsed state. We study how the capture rate

depends on the swelling period and gel-nanoparticle interactions and we quantify the optimal swelling period which maximizes capture rates.

SESSION BM03.03: Poster Session: Multiscale Modeling of Soft Materials and Interfaces
Session Chairs: Sanket A. Deshmukh, Meenakshi Dutt and Yang Zhang
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

BM03.03.01
Confinement Effect of Nanoscale Biological Systems Arvand M. Navabi and Nima Rahbar; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

The nanoscale molecular dynamics of the confined organic matrix in the biological material, nacre and its contribution to the exceptional toughness of this biomaterial has been studied. While under stress, the dynamics of the nanoscale structure of nacre have significant influence on the energy dissipation of the system and ultimately on the fracture toughness of the material. For better understanding these mechanisms, a solution of the c-domain consensus of the protein, Lustrin A, was confined between two ceramic layers of aragonite by employing molecular dynamics computations. Then the aragonite walls were subjected to shear, and the polymeric system responded by unfolding. This study reports increase in the energy dissipated through unfolding mechanisms of the protein system as the confinement size decreases. The dominant energy dissipation method in larger systems transition from unfolding to polymeric interactions and entanglements.

BM03.03.02
2D Powerless Capillary Microchannel Device for Efficient Capture of Circulating Tumor Cells Yiting Zheng; Northeastern University, Boston, Massachusetts, United States.

Introduction: Liquid biopsy of circulating tumor cells (CTCs) can help find cancer at an early stage and determine whether treatment is effective or not. Secondary microscale features such as micropillars, microstripes and silicon nanowires, microfluidic channels can be functionally modified with cell selective species such as anti-epithelial cell adhesion molecules (Anti-EpCAM) and aptamers to enhance efficacy of CTC capture. However, the surface bound cell adhesion molecules have less flexibility to interact with receptors over-expressed on the surfaces of flowing cancer cells, leading to low capture efficiency. Meanwhile, the microfluidic devices require sophisticated processes to make and accessory such as pumps and tubing to work, which makes microfluidic device not an ideal tool for point-of-care diagnosis and prognosis.
This work describes a method for efficient capture of CTCs from human whole blood using a two dimensional (2D) capillary microfluidic device modified with long chain polymers that have cell-adhesive terminals. The height of microchannel is designed to approximate the diameter of single cells. Given its low cost, easy operation, repeated usage, and zero-power consumption, this device would find its use at points-of-care.
Results: CEM cells solution with PBS was studied in channels with different heights and capture efficiency is inversely proportional to channel height to the second power which agrees well with the modeling of cell sedimentation in channels. Cells are injected in channels by flow and the flow filling time in our device is not long enough to let all the cell settling. The 30 μm channel can achieve 95% capture efficiency. This optimal parameter was applied in cell capture in human blood. Figure 2 shows fluorescence images of CEM cells captured on folic acid modified channel The capture efficiency of the channel has calculated to be $88.3 \pm 14.6\%$ for CEM cells in spiked blood with concentration of 5×10^6 cell/ml and $90\pm4\%$ with concentration of 5,000 cell/mL. CEM cells are found firmly attached on the substrate. The capture efficiency agrees well with the assumed theory of cell rolling and cell sedimentation.
Conclusions: Circulating tumor cells (CTCs) spiked in human blood can be captured efficiently with 2D capillary microchannel device which was modified with polymer brush. Blood or cell suspension can be sucked in the channel by capillary force. The kinetics of channel filling for buffer solution containing cells agreed with theoretical models. The capture efficiency decreases with increased height of channel due to cell rolling and tethering in microchannels. In high channel, less cells are captured by cell rolling and tethering while more cells have ligand receptor reaction by cell settling. The polymer brush modified glass can be easily dissembled for further analysis of captured cells. This non-sealing and pump-less device does not have blocking or leaking problems as normal fluidic device.

BM03.03.03
The Effect of Microenvironment Stiffness on Oligodendrocyte Differentiation Alexander Evenchik; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Understanding how a cell senses its environment is key to understanding how it acts and responds to different stressors, such as changes of pH, temperature, or concentration of small molecules. Oligodendrocytes are a type of glial cell found in the central nervous system; they are responsible for wrapping axons in myelin, a sheath that allows neurons to effectively transmit electrical impulses in the brain. Oligodendrocyte dysfunction leads to debilitating diseases such as multiple sclerosis. Polystyrene petri dishes, which are currently used to culture and study these cells, are poor models of the brain (e.g. the Young's Modulus of polystyrene is approximately 10^6 times larger than that of the brain). It is hypothesized that this lack of biomimicry may contribute to inaccurate or incomplete understandings of oligodendrocyte and myelin biology, as well as hinder the pace of therapeutic development. The goal of this research is to help bridge that gap of understanding by studying the effect of various mechanical cues on the differentiation and myelination of human oligodendrocyte cells. Here we fabricate and characterize various substrates that recapitulate key physical properties of the oligodendrocyte microenvironment. Human oligodendrocytes are derived from induced pluripotent stem cells and cultured in these engineered microenvironments. The extent of differentiation and myelination is assessed via immunocytochemistry and fluorescence microscopy. These results may help lead to more effective methods to culture human oligodendrocytes, and shed light on how these cells may respond to pathological mechanical changes in the *in vivo* environment.

BM03.03.04
Continuous Elasto-Capillary Clustering of Tilted Nano-Pillars Sang Moon Kim[5], Junsoo Kim[1], Seongmin Kang[2], Daeshik Kang[3], Segeun Jang[7], Seung Eon Moon[6], Hong Nam Kim[7] and Hyunsik Yoon[4]; [1]Harvard University, Massachusetts, Massachusetts, United States; [2]Chungnam Univ., Daejeon, Korea (the Republic of); [3]Ajou Univ., Seoul, Korea (the Republic of); [4]Seoul National University of Science and Technology, Seoul, Korea (the Republic of); [5]Incheon National University, Incheon, Korea (the Republic of); [6]Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of); [7]Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Complex structures of clustered micro/nano pillars from the elastocapillarity have been extensively studied for the application of mechanical electrical micro system devices and sensors systems. Herein, we investigate the unidirectional clustering property of initially slanted nanopillars. The deionized water droplet was dispensed onto the slanted nanopillars fabricated by using of Faraday cages and was dried off to generate cluster formation of the patterns. We observed non-continuous clustering of the low-tilted (initial tilting angle of ~0° and ~15°) nanohairs and unidireictional clustering of the nanopillar arrays with tilting angles of ~30° and ~45°. We proposed theoretical model to analyze the unidirectional cluster formation and set a criterion for a unidirectionality. Furthermore, we predicted the shape of clustered pillars for the case of the non-continuous clustered pillars based on our proposed model.

BM03.03.05
Investigation of Self-Assembly of Polypeptoids in Aqueous Solution—From Atomistic to Coarse-Grained Simulations Pu Du and Revati Kumar; Louisiana State University, Baton Rouge, Louisiana, United States.

Polypeptoids or poly N-substituted glycines are a type of peptidomimetic polymers that are highly tunable, and hence an ideal model system to study self-assembly as a function of chemical groups in aqueous soft matter systems. In this study, atomistic simulations were performed on sequence-defined ionic peptoid block copolymers consisting of a hydrophobic and a hydrophilic segment (with one singly charged and the remaining uncharged polar groups) in aqueous solution. These studies revealed that the placement of the charged moiety on the polymer chain affected the micellar structure and shape. However, the computational expense limits simulation times and system sizes to a hundred nanoseconds and tens of nanometers, respectively, necessitating the development of coarse-grained models to study more complex polypeptoids with multiple types of hydrophilic side groups. A coarse-grained (CG) model for N, N-dimethylacetamide (DMA), which represents the polypeptoid backbone, is developed as a step towards developing a CG model of the complex polypeptoids system. The DMA CG model is parameterized to reproduce the structural properties of DMA liquid as well as a dilute aqueous solution of DMA using a reference all atom model, namely the OPLS-AA force-field. The intermolecular forces are represented by the Stillinger-Weber potential, which consists of both two- and three-body terms that are very short-ranged. The model is validated on thermodynamic properties of liquid and aqueous DMA, as well as the vapor-liquid interface of liquid DMA and the structure of a concentrated aqueous solution of DMA in water. Without long-ranged interactions and the absence of interaction sites on hydrogen atoms, the CG DMA model is an order of magnitude faster than the higher resolution all-atom (AA) model.

BM03.03.06
Artificial Exosomes—Tailored Conjugation of Fusogen to Lipid/Polymer Hybrid Vesicles for Enhanced Drug Delivery Jeong Yi Kang[1] and Jin Woong Kim[1, 2]; [1]Bionano Technology, Hanyang University, Ansan, Korea (the Republic of); [2]Chemical and Molecular Engineering, Hanyang University, Ansan, Korea (the Republic of).

The development of a wide spectrum of nanoscale technologies is beginning to change the scientific landscape in terms of disease treatment. The small size, customized surface, improved solubility, and multi-functionality of nanoparticles will continue to open many doors and create new biomedical applications. Indeed, the novel properties of nanoparticles, including carbon nanotube, nanofibers, self-assembling polymeric constructs, liposome, and nano-sized silicon chips, offer the ability to interact with complex cellular functions in new ways. Among them, recent technology pays attention to exosomes, nano-sized vesicles that are released from various types of cells into the extracellular space, since they are able to provide a practical means of intercellular communication and transmission of macromolecules between cells. Moreover, they are able to act as useful vectors for drugs because they are composed of cell membranes, rather than synthetic polymers, and as such are better tolerated by the host. In this study, we propose an exosome-analogous drug delivery system which is established by using lipid/polymer hybrid vesicles with fusogenic peptide conjugates. The lipid/polymer hybrid vesicles are fabricated by co-assembly of phosphatidylcholine and poly(ethylene oxide)-*b*-poly(caprolactone)-*b*-poly(ethylene oxide). Thanks to large size and slow dynamics of amphiphilic triblock copolymers at the bilayer membrane, the hybrid vesicles show long-circulating time and high drug loading efficiency. Fusogenic peptide, penetratin, induces vesicular interaction with cell membrane, thus enhancing cellular uptake. To evaluate the cell affinity of fusogenic exosomes, the interaction force between an exosome and a cell is characterized *via* microscale thermophoresis. Finally, *in vitro* cell-penetration study demonstrates the practical applicability of our artificial exosome as a remarkable cell delivery nanocarrier.

BM03.03.07
Systematic Control of Flory-Huggins Interaction Parameter of Block Copolymer Forming Sub-10 nm Perpendicular Lamellar Pattern Seung Won Song, Yoon Hyung Hur and Yeon Sik Jung; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Directed self-assembly of block copolymer is one of the most promising candidates for sub-10 nm scale lithography due to its cost effectiveness and nanometer scale pattern resolution. However, further improvements of line edge fluctuation and pattern resolution to sub-10 nm region of Poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) block copolymer remain as critical challenges. To improve pattern resolution, higher Flory-Huggins parameter (χ) is required. However, too high of χ value induces horizontal lamellar pattern which cannot be used in devices. Therefore, deliberate design of block copolymer with medium χ value is required so that χ value is high enough to achieve sub-10 nm pattern formation and small enough to prevent horizontal lamellar pattern. Here, we suggest a newly designed block copolymer that can form sub-10 nm perpendicular lamellar pattern which is aligned by graphoepitaxy template. The block copolymer was synthesized by reversible addition-fragmentation chain-transfer polymerization copolymerized with fluorine containing monomer, which is hydrophobic. The modified block copolymer showed controlled χ value as the fraction of hydrophobic monomer changed. Block copolymer pattern with sub-10 nm feature size could be achieved due to a three times higher χ value than the conventional PS-*b*-PMMA. Even though the newly synthesized block copolymer has a high χ value, the polymer could form perpendicular lamellar morphology by short thermal annealing.

BM03.03.08
Theranostic Pluronic Nanoparticles for Glioblastoma Treatment—Synergic Application of Chemotherapy and Photodynamic Therapy Diogo S. Pellosi[1], Leonardo B. de Paula[2], Maryanne T. de Melo[2], Danielle R. Mota[1], Giovanni A. Lima[1] and Antonio C. Tedesco[2]; [1]Chemistry, Federal University of São Paulo, Diadema, Brazil; [2]Chemistry, University of São Paulo, Ribeirão Preto, Brazil.

Despite advances in the fight against cancer, glioblastoma multiform treatment continues inefficient due inhibitory activity of brain-blood barrier (BBB) that causes low efficacy and selectivity for temozolomide (TMZ) chemotherapy. In order to improve therapeutic outcomes aiming side effects reductions the present work followed two strategies: (i) the use of theranostic pluronic nanoparticles and (ii) application of photodynamic therapy (PDT) as adjuvant treatment. Pluronic P85/F127 nanoparticles were engineered as multifunctional theranostic/targeted nanoparticles (*m*-NP) through the chemical functionalization of its surface with biotin (target moiety) and rhodamine-B (fluorescent probe). The chemical-modified pluronic copolymers self-assembly into *m*-NP that present the advantage of overcoming BBB and encapsulate multiple cargo for the application of multiple tumor treatment modalities with an optimized drug ratio. In addition, PDT characteristics such as its high selectivity upon light-driven activation and the non-development of cross-resistance mechanisms make it a valuable option as adjuvant for TMZ chemotherapy. *m*-NPs formulations were firstly optimized to obtain best drug loading conditions (for both TMZ and PDT agent) and formulation long-term stability. In these studies we demonstrated that lyophilization of formulation was the

best methodology to obtain a longer shelf life for the proposed system. Due theranostic characteristics of *m*-NP and PDT agent, *in vitro* confocal microscopy studies on U87-MG, T98-G, U343 glioblastoma cells and NHI-3T3 fibroblast as control were evaluate in order to understand *m*-NPs role in uptake and intracellular drugs distribution. Uptake experiments demonstrated that the proposed nanoparticle possess higher affinity toward cancer cell lines in detriment of the non-tumor cell line NHI-3T3. In addition, confocal images revealed a broad intracellular distribution for both *m*-NP and encapsulated drugs at cells cytoplasm, but not in the nucleus. Blank formulations were not cytotoxic while formulations containing TMZ or PDT agent separately presented a reduced effect in cell viability. Nevertheless, PDT/TMZ concomitant treatment presented high efficiency due their synergic action even at low and safe drug concentrations. As demonstrated by flow cytometry experiments, this synergism is due to the different mechanisms of action of each proposed drug in the cell cycle arrest and their selective/controlled delivery at the intracellular level. In conclusion, these results point *m*-NP are a promising nanostructure to carry different drugs and selectively release encapsulated cargo in cancer cells.

BM03.03.09
Computational Design of Dendron-Grafted Soft Materials-Based Nanoparticles Akash Banerjee and Meenakshi Dutt; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Many drug delivery strategies demand the need for the adsorption and transport of charged, therapeutic biomolecules. These requirements can be met by nanoparticles (NPs) encompassing multiple molecular species that endow electrostatically-induced interfacial binding of specific biomolecules. We are interested in understanding the role of the architecture and composition of the molecular species on the morphological characteristics of the NPs. We study multicomponent NPs encompassing phospholipids and lipids bearing hyper-branched polyelectrolytes (namely, polyamidoamine (PAMAM) dendrons) via the Molecular Dynamics simulation technique. The bonded and non-bonded interactions between the particles is captured by the Martini force field. We examine the impact of interfacial area, dendron generation and relative concentration on the NP morphology. Our studies can potentially guide the design of multicomponent amphiphile-based nanoparticles for applications in medicine and environmental sustainability.

BM03.03.10
A Multiscale Approach to Study Molecular and Interfacial Characteristics of Colloids Xiang Yu and Meenakshi Dutt; Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

The functions of colloidal particles are dictated by interfacial properties which are determined by an interplay of physical interactions and processes spanning multiple spatiotemporal scales. The multiscale characteristics of colloidal particles can be resolved by the hybrid Molecular Dynamics- Lattice Boltzmann technique. This technique enables the resolution of the particle dynamics along with long range electrostatic and hydrodynamic interactions. We have examined the feasibility of an implementation of the hybrid technique to capture the molecular and interfacial characteristics of colloidal particles, such as vesicles. For simplicity, we have examined two types of vesicles whose molecular components have different sustained interactions with the solvent. One of the vesicles encompassed phospholipids and the other vesicle was composed of phospholipids and poly ethylene glycol (PEG)-grafted lipids. The molecular and interfacial characteristics of the phospholipid vesicle and PEGylated, or hairy, vesicles are found to be in good agreement with earlier experimental, computational and theoretical findings. These results demonstrate that the multiscale hybrid technique is suitable for capturing the molecular and interfacial characteristics of colloidal particles. The results of our investigations demonstrate the potential of the hybrid technique in capturing multiscale interfacial characteristics of intra- and inter-colloid interactions in suspensions under different flow conditions, and their relation to molecular properties.

BM03.03.11
Rational Surface-Anchored Cross-Linking of Nanogel Framework for RhD-Epitopes Stealth Red Blood Cells Yueqi Zhao, Mingjie Fan, Ben Wang and Ruikang Tang; Zhejiang University, Hangzhou, China.

The Rhesus D (RhD) as well as A and B antigens are important immunogenic epitopes on red blood cells (RBCs) which need type matching during blood transfusion, and mismatching will lead to fatal reactions. Producing antigen negative RBCs, which are universal for transfusion, are necessary especially in emergent situation. While the conversion of A and B antigens into immunity negative cells have been achieved, however, the transition of D-positive cells to D-negative is still problematic. To solve the problems in transfusion, we developed a rational approach to shield the antigens on the Rh D-positive RBCs for D-negative blood production by using the surface-anchored and cross-linked nanogel framework. A thin and uniform nanogel layer,which is consisted of alginic acid and tyramine, was constructed on individual RBCs catalyzed by surface-anchored enzyme. The physical and biological properties of modified RBCs were similar with native RBCs. More importantly, the D antigens on surface of engineered RBCs were shielded completely by the framework layer, preventing the recognition of immune system both in vitro and in vivo. The distribution of "the D-negative blood" in tissues including heart, liver, spleen and kidney was similar with native ones in blood circulation. The resulting stealthy effects achieve complete sheltering of blood group D antigens on RBCs membrane, providing a potential methodology of cell surface engineering for universal blood transfusion regardless of blood types.

BM03.03.12
Lipid Morphology in Solid Lipid Nanoparticles Demi L. Pink[1], Jayne Lawrence[2, 1] and Christian D. Lorenz[1]; [1]King's College London, London, United Kingdom; [2]University of Manchester, Manchester, United Kingdom.

Solid lipid nanoparticles (SLN) first came to attention in 1991 as they were considered promising particles to investigate with regards to potential applications in drug delivery. These nano-colloidal particles are typically spherical and are comprised of a solid lipid core. This solid lipid core is not perfectly crystalline and so it contains defects which can be used to trap and solubilise lipophilic and hydrophobic drug molecules. Surfactant molecules are then utilised to further stabilise the lipid core. The exact properties of SLN depend on their composition and preparation, with lipid and surfactant selection being key in the development of non-toxic, stable nanoparticles. Since SLN properties can be modified by using different lipids and surfactants, SLN can be optimised for encapsulation and delivery of specific molecules. Whilst the potential for their use in healthcare has been the dominant area of research, there are also options for the application of SLN in a range of other industries, including cosmetics and agriculture.

A significant challenge concerning the use of SLN in drug formulations is the tendency of the solid lipids to converge towards a perfectly crystalline lattice when stored over time. This is due to the increased thermodynamic stability this confers. However, the transition towards a perfect crystalline lattice removes the defects in which the drug molecules are stored. This can result in the expulsion of the drug molecules during storage or rapid expulsion of the drug upon administration, potentially rendering them ineffective. The triglycerides used in SLN can exist in 4 distinct conformations and by examining the conformations of triglyceride in the SLN we aim to better understand the mechanisms behind drug encapsulation and drug expulsion.

This work uses molecular dynamic simulations to investigate the overall morphology of the SLN as well as looking closely at the conformation of lipids in solid lipid nanoparticles. Through this we have gained a detailed understanding of the role of lipids within SLN. By modifying the temperature of our simulations we were able to compare the conformations of lipids in both liquid and solid lipid aggregate as well as in the SLN. This simulation worked is paired with experimental work in order to develop a multi-scale and experimentally relevant understanding of solid lipid nanoparticles.

BM03.03.13
Design Guidelines of Optoelectronics Devices Based Triboelectrification <u>Abdelsalam Ahmed</u>[1], Islam M. Hassan[1], Ali Radhi[1] and Jean Zu[2]; [1]University of Toronto, Toronto, Ontario, Canada; [2]Stevens Institute of Technology, Hoboken, New Jersey, United States.

Triboelectric nanogenerators (TENGs) are a new power generation technology with high affinity to ambient energy harvesting from the surrounding media. This has driven many researchers towards coupling such technologies into numerous electronic devices, introducing the field of triphototronics. An analytical framework has been established for practical evaluation of the multiphysics aspects of triphototronics devices. The work shows the numerous operating modes of TENGs and their impact on the electrical performance from structural, material and ecological perspectives. Scalability, electrical regulatory systems, supply channel control features are presented. The attributed properties of lightweight, low-cost, high material selections will be shown to have a significant impact on triphototronics devices.

BM03.03.14
Corrosion Modelling of Ti-20Zr in Body Environment Conditions <u>Julia Mirza Rosca</u>[1], Hosam Sakr[1], Alexandru Pascu[2] and Elena Stanciu[2]; [1]Mechanical Engineering Department, University of Las Palmas de Gran Canaria, Las Palmas de GC, Spain; [2]University Transylvania of Brasov, Brasov, Romania.

Zr alloy was evaluated because it has been suggested as a candidate for human body implant material and was primarily developed in response to concerns of potential cytotoxicity and adverse tissue reactions caused by vanadium and aluminium in the actually used biomaterial Ti-6Al-4V.

The Ti-20Zr alloy (donated by RD&D, Bucharest, Romania) was obtained by vacuum melting. The cylindrical electrodes were obtained and embedded in a resin. The specimens are ultrasonically cleaned using deionized water, and etched in Kroll reagent containing 10 ml of HF, 5 ml of HNO$_3$ and 85 ml of water for microscopic observation, using an Olympus PME 3 – ADL microscope.
The microstructure and microhardness were determinated and the tensile strength was evaluated. The electrochemical behaviour has been evaluated in simulated body fluid (SBF) using Electrochemical Impedance Spectroscopy technique (EIS).

From metallographical images can be observed that the sample has an alpha-beta structure.
From microhardness measurements can be concluded that the alloy formed a hard layer on its surface which greatly improves the wear resistance.
The alloy exhibits brittle fracture and yield stress was equated to ultimate tensile stress. The obtained tensile strength can be considered good in relation with other similar implant materials.
The impedance spectra were fitted with two time constants equivalent circuit and the fitting parameters indicate long-term stability of the passive layers in surgical implant conditions.

The results were confirmed by mechanical approach, in terms of two-layer model of the oxide film, consisting of a thin barrier type inner layer and a porous outer layer. The pronounced porous outer layer is expected to facilitate the incorporation of mineral ions and to improve the resistance to electrochemical corrosion over the potential of relevance for human body conditions.

BM03.03.15
MD Simulation and Cellular Potts Model for Neuronal Differentiation on Polymeric Nanoscaffolds <u>Wu Qi</u>[1], Pegi Haliti[1], Debika Debnath[1], Bhushan Dharmadhikari[2] and Prabir Patra[1]; [1]Biomedical Engineering, University of Bridgeport, Bridgeport, Connecticut, United States; [2]Electrical Engineering, University of Bridgeport, Bridgeport, Connecticut, United States.

Over the past decades, a great progress has been made in the field of tissue engineering and regenerative medicine especially in the differentiation and proliferation of stem cells into desired lineages in vitro on 2D scaffolds. The purpose of this study is to simulate and design of nanofibrous Polycaprolactone-Graphene (PCL-G) scaffolds, for neuronal differentiation and investigate subcellular and cellular level interactions of cells with the scaffold using MD simulation and Cellular Potts Model (CPM). We explore the interactions between PCL, graphene, and F-actin towards better understanding of neuron cell mobility on PCL-G scaffold. F-actin protein is associated with controlling the mobility and influences the dendritic spines for neuronal cell. Here we use VMD (Visual Molecular Dynamics) for modeling and visualization, NAMD for Molecular Dynamics (MD) computations and Cellular Potts Model (CPM) for cell-cell, cell-scaffold interaction study. After 10ns of MD simulation data and trajectory visualized in VMD, we observed that PCL chains shows affinity towards graphene sheet and try to fit into the graphene sheet. Further, we plan to repeat MD simulations using different sizes of graphene sheet allowing further to investigate the interactions between F-actin and PCL-G. For the CPM simulation, the interactions such as cell-cell, cell-scaffold adhesion and cellular motility contribute to the system's energy given by a function known as Hamiltonian which manages the lattice rearrangement using the stochastic Monte Carlo's probabilistic model by minimizing the system's total energy. In our simulation we set 1 pixel to correspond to 4μm and the time, which is given by Monte Carlo Steps (MCS), to corresponds to 2s of the real experimental time. One simulation is set for as long as 12h to also consider that cells can undergo duplication or apoptotic events. We found out that the cells are moving and changing their shapes, their mobility and growth. More investigations are underway on altering cell-cell and cell-scaffold adhesion energy that can be the key on achieving an alignment of cells on the scaffold and migration afterwards.

BM03.03.16
Supercoiled DNA with Mismatched Base Pair—Probing the Role of Structural Defect on Plectoneme Pinning by Molecular Dynamics Simulation <u>Parth Rakesh Desai</u>[1,2], Siddhartha Das[1] and Keir C. Neuman[2]; [1]Department of Mechanical Engineering, University of Maryland, College Park, College Park, Maryland, United States; [2]NHLBI, National Institutes of Health, Bethesda, Maryland, United States.

Mismatched base pairs in DNA can result in mutations. Mismatched base pairs are recognized by the MutS enzyme, which initiates the mismatch repair pathway. MutS recognizes mismatches through a process that involves introducing a sharp bend and flipping out a DNA base at the mismatch site. Single-molecule magnetic tweezers-based DNA supercoiling measurements found that plectonemes nucleate, and are localized, at a mismatch. Localizing the mismatch at the end of the plectoneme loop may facilitate mismatch detection by MutS due to the stabilization of the bent and base-flipped out configuration. The plectoneme end loop containing a mismatch can kink more easily, which reduces the energy of the end loop. However, these experiments were limited to positively supercoiled DNA at salt concentrations of 0.5 M NaCl and higher. Theoretical studies predict that for positively supercoiled DNA under physiologically relevant conditions, *i.e.*, at salt concentrations of 0.2 M NaCl, plectoneme nucleation at the mismatch becomes probabilistic rather than deterministic. Here, we use molecular dynamics simulations to study the effect of a mismatched base pair on DNA supercoiling. We employ the oxDNA model to simulate DNA under torsional stress. The oxDNA model is a coarse-grained model in which each nucleotide is treated as a rigid ellipsoid with three interaction sites. The oxDNA model has been shown to accurately reproduce the response of an intact DNA to both negative and positive torsional stress. To model a mismatched base-pair we eliminate hydrogen bonding between the two nucleotides. Using this modification of the oxDNA model, we first determine the effect of a mismatched base-pair on the bending free energy of a short 15 base-pair DNA and compare the results to

atomistic simulations. We find that the bending free energy of a short DNA containing a G-T mismatch is close to the bending free energy predicted by atomistic simulations. We then perform simulations of a 600 base-pair DNA with 0, 2, 4 and 6 consecutive mismatched based pairs. We find that for positively supercoiled DNA at high salt, *i.e.*, 1 M NaCl, the plectoneme always localizes at the mismatch, in good agreement with experiments. Extending this framework to study the case of both positively and negatively supercoiled DNA at 0.2 M NaCl, we find that plectoneme localization at the mismatch indeed becomes probabilistic. We will present the relation between the probability of plectoneme localization and the number of mismatches in addition to an analysis of the shape of end the loop of the plectoneme for different mismatches.

BM03.03.17
Bioinspired Multifunctional Surfaces for Versatile Optical Applications <u>Seongmin Kang</u>; Chungnam National University, Daejeon, Korea (the Republic of).

The capability of fabricating multifunctional polymeric structures has great advantages to satisfy the increasing demand for flexible and wearable energy conversion devices, electronics and displays. In this work, we have demonstrated a novel fabrication method for structuring bioinspired multifunctional moth-eye TiO_2/PDMS pad by using conventional lithography, imprinting, and thin sacrificial layer. It is noted that the embedded TiO_2 nanoparticles acted as an effective UV-protector. As a result, the high energy UVB-light is perfectly blocked by the embedded TiO_2 nanoparticles and the UVA-light is partially penetrated though the surface. Also, the moth-eye inspired nanostructures on the surface show high transparency in a visible wavelength range as well as self-cleaning effect due to nano-roughness on the surface. Further, we successfully fabricated hierarchical structured surface, where we want, by controlling partially-cured region using the multifunctional polymeric pad with partial blocking property of UVA ray.

BM03.03.18
Temperature-Independent Zero-Birefringence Polymer and its Compensation Mechanism for Temperature Dependence of Birefringence <u>Kenji Wada</u>[1], Akihiro Tagaya[1] and Yasuhiro Koike[1, 2]; [1]Graduate School of Science and Technology, Keio University, Yokohama, Japan; [2]Keio Photonics Research Institute, Kawasaki, Japan.

Optical polymers are used as key materials for liquid-crystal displays (LCDs) due to their ease of processing, high transparency, and low-cost. Most of polymers exhibit orientational birefringence because polymer chains tend to become oriented by processing. In LCDs, the birefringence in polarizer protecting films cause light leakage. This light leakage decreases the contrast ratio and increases color shift depending on the viewing angle. Therefore, orientational birefringence of the polymers is ideal to be zero for LCDs. Orientational birefringence is always zero no matter how much a polymer is orientated by processing if intrinsic birefringence Δn^0 which is a specific value of each polymer is zero. Our group proposed and synthesized zero-birefringence polymers (ZBPs) which exhibited almost no Δn^0 [1]. Recently, we found temperature dependence of Δn^0 of the polymers [2]. It becomes a problem for in-car LCDs which generally require no birefringence in the large temperature range from around −40 to 85°C, compared with the range for interior LCDs. However, the mechanism of temperature dependence of Δn^0 has not been clarified. For synthesis of temperature-independent zero-birefringence polymers (TIZBPs) which exhibited almost no Δn^0 in the wide temperature range, the detail clarification of the behaviors of polymer molecules is necessary. The purpose of this article is clarification of the mechanism of temperature dependence of Δn^0 for design and synthesis of TIZBP by the method of birefringence compensation.
Poly(methyl methacrylate (MMA) /benzyl methacrylate (BzMA)) and poly(MMA/phenyl methacrylate (PhMA)) in various composition ratios were synthesized. Then, uniaxial heat-drawn films of these copolymers were made. Absorbance spectrums in IR region of the copolymer films were measured from 25 to 65°C by FT-IR. The spectrums were analyzed to clarify the behavior of main chains and side chains of the polymer in the heating process. Also, Δn^0 of the films from 15 to 65°C were evaluated by automatic birefringence measurement system to calculate temperature dependence of Δn^0 of them. From the above, it suggested that increasing or decreasing of Δn^0 in heating process is related to the orientation behavior of a polymer molecule. Based on the results, the composition of monomers in a system of MMA, BzMA, and PhMA was calculated to compensate birefringence and its temperature dependence for designing a TIZBP. Moreover, poly(MMA/BzMA/PhMA) (39/38/23 wt.%) was synthesized and exhibited almost no intrinsic birefringence Δn^0 from 15 to 65°C.

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BM03.03.19
All Atom and Coarse-Grained Molecular Dynamics Simulations of an Interdigitated Multilamellar Phase of a Mixed Surfactant System <u>Arpita Srivastava</u> and Ananya Debnath; Indian Institute of Technology, Jodhpur, Jodhpur, India.

A coarse-grained (CG) molecular dynamics simulation of a cationic surfactant behenyl trimethyl ammonium chloride (BTMAC), co-surfactant (SA) in presence of water is performed at a ratio of 2:1 at 283 K from an all atom (AA) simulation [1]. The CG bonded potentials are derived by the Boltzmann inversion of their respective AA distributions [2]. A good match in the CG and AA bonded distributions validate the bonded potentials derived for the model. The MARTINI non-bonded potentials [3] are used to obtain the interdigitated ($L_{\beta i}$) multi-lamellar phase as in the AA simulation. The single chain conformational entropies of both BTMAC and SA reveal that around 4% of the molecules have relatively higher entropy than the rest of the molecules, indicating coexistence of both ordered and disordered phases in the bilayer. The molecules with higher entropy and low order parameter are confined to the upper monolayer of a bilayer without flipping to the other layer as evident from their cosine angles with respect to the bilayer normal. The coexistence between ordered and disordered phases is attributed to the oscillation between the bent and stretched conformers of disordered BTMAC molecules with an energy barrier of 5 kJ/mol whereas all ordered molecules stay stretched throughout the simulations. Our calculations show the suitability of MARTINI force field in predicting the phase behavior of interdigitated bilayer and reveal that the coexistence of two phases arise due to the strong interdigitation between two layers dictated by the chain length of shorter SA which do not allow longer BTMAC to flip-flop and traverse. Thus our analysis will be helpful in understanding the multi-component membrane dynamics with various applications in the field of biological membranes, pharmaceuticals or industry.

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BM03.03.20
Mechanical Basis for the Morphology of Fibrillar Aggregates Thomas C. Michaels and L Mahadevan; Harvard University, Cambridge, Massachusetts, United States.

The self-assembly of fibrillar aggregates is of importance in biology, biomedicine and materials science, yet understanding the range of possible shapes for these structures remains an open question. We propose a coarse-grained approach that averages over specific molecular details to suggest that the spatial complexity of self-assembling fibrillar structures is due to the competing effects of (the bending and twisting) elasticity of individual filaments and the adhesive interactions between them. We show that a theoretical framework accounting for this allows us to capture a number of diverse fibril morphologies observed in natural and synthetic systems, ranging from Filopodia to multi-walled carbon nanotubes, and leads to a phase diagram of possible fibril shapes. We also show how the extreme sensitivity of these morphologies can lead to spatially chaotic structures. Together, these results suggest a common mechanical basis for the microscale fibril morphology as a function of the nanoscale mechanical properties.

BM03.03.21
Crack Formation in Wet Colloidal Pillars Justin Beroz, Alvin Tan, Ken Kamrin and A. John Hart; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

A basic and well-established assumption about solid materials is that they do not crack when subject to uniform compression. Intuitively, it is paradoxical to imagine how a solid material could conspire to split apart while being uniformly compressed together. In this talk, we present an example of such a case, wherein cracks appear during the drying of vertically freestanding water-saturated colloidal pillars we constructed using a direct-write technique. Paradoxically, the cracks form at the free end, far from the substrate, where the particle network is unconstrained in contracting its volume as it bears compression by a uniform capillary pressure acting at its outer surface. We first detail our experiment results and then provide a theoretical explanation for the cracks based on a dominant balance of wetting energy terms, from which follows a simple relationship between the colloid particle size and pillar dimensions that captures the presence or absence of cracks. Our theoretical result agrees with experiment, and demonstrates that having an evaporating liquid exert the pressure is fundamentally different compared to the typical balance of surface energy and bulk stress considered for dry materials.

BM03.03.22
sasPDF—Pair Distribution Function (PDF) Analysis of Nanoparticle Assemblies Chia-Hao Liu[3], Ellie Buenning[1], Eric M. Janke[2], Igor Coropceanu[2], Dmitri V. Talapin[2], Sanat K. Kumar[1] and Simon J. Billinge[3, 4]; [1]Chemical Engineering, Columbia University, New York, New York, United States; [2]Chemistry, The University of Chicago, Chicago, Illinois, United States; [3]Applied Physics and Applied Mathematics, Columbia University, New York, New York, United States; [4]Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York, United States.

Nanoparticle superlattice assemblies (NPSA) are being developed for their special properties in applications such as flat-panel displays. The properties of the resulting assemblies can be further engineered by controlling interparticle spacings and arrangements. It is therefore crucial to be able to determine the structure of these NPSAs as quantitatively and accurately as possible. In general, they may have only short-range (on the nanoparticle length-scale) structural correlations (though some assemblies are highly crystalline), making the quantitative determination of NPSA structure difficult. TEM is popular for visualizing mesoscopic structures. Small angle scattering (SAS) may also be applied. However, conventional analysis of SAS data as so far resulted only in semi-quantitative analyses and TEM images can be subjected to sample bias and are not suitable for sample-average measurements. Atomic pair distribution function (PDF) analysis of x-ray and neutron powder diffraction data is a powerful approach for studying non-periodic structural signals, for example from nanoparticles themselves. It yields local structural information from nanomaterials with high precision and quantitative accuracy. Here we describe how have extended the PDF analysis to the SAS regime, where we can apply similar quantitative modelling methods that are proving powerful at the atomic scale, but to the extraction of structural information about superlattice assemblies. In this presentation, we will present PDF analysis in SAS regime (sasPDF) and we will also present applications of sasPDF techniques to systems with different levels of ordering, from highly crystalline assemblies to isotropic, amorphous polymer coated silica nanoparticles that have promise in gas separation membranes.

BM03.03.23
Synthesis of Metal and Polymer Nanoparticles for Hybrid Nanoassembling and Functional Properties Nikunjkumar Visaveliya; The City College of New York, New York, New York, United States.

Nanoscale metal and polymer particles have captured broad attention and allowed enormous technological progress in various fields from biomedical and photonics to catalysis and sensing. In this work, surface-active polymer nanoparticles as well as polymer-polymer and polymer-metal nanoassembly particles are synthesized, and different parameters such as their size, morphologies and assembling strength have been studied. Nanoassembly particles are attractive because of the coupled properties with a large surface to volume ratio. A key challenge is to produce the core shell polymer nanoparticles via single-step processes. To address this concern, here, microfluidics approach and precise interfacial reaction strategies is highly promising, and hence different types of surface layered polymer nanoparticles were obtained in one-step processes. An inner core material is hydrophobic whereas a hydrophilic surface layer (in-situ formed during the polymerization process) swells in the aqueous environment. On other side, polymer-metal nanoassembly particles as well as metal catalyzed metal deposited four layered nanoassembly particles of tuned size and compositions were produced. It is shown that these particles can be used as nano-sensor particles for surface-enhanced Raman spectroscopy.

BM03.03.24
Toward Self-Healable Multifunctional Coatings Containing Catechol in Hybrid Polysilsesquioxane Sohyeon Park, Sungwon Jung and Jinkee Hong; Chemical and Biomolecular Engineering, Yonsei University, Seoul, Korea (the Republic of).

The polysilsesquioxane (PSQ) is an organic/inorganic hybrid material and has excellent biocompatibility and mechanical properties. Thus, PSQ is regarded as a promising candidate for coating materials for various medical devices. From a medical device point, the ideal coating should have the ability to exert excellent biocompatibility, durability, antimicrobial effect and drug delivery capabilities. However, most of the developed coatings for medical devices were limited in exhibiting this simultaneous ability. Here, we fabricated catechol-functionalized PSQ hybrid coatings with various functions. First, well-defined PSQ matrixes were synthesized by sol-gel reaction using hydrophilic precursors, and catechol groups were functionalized in carboxymethyl cellulose (CMC). Subsequently, the catechol-functionalized PSQ hybrid coatings were prepared by excellent compatibility of organic primers in PSQ to catechol-functionalized CMC. Synthesized PSQs were highly durable and exhibit superhydrophilic properties that contribute to the antimicrobial effect, through their morphological changes. On the other hand, the catechol residues of the coating were initiated and promoted by rapid and strong hydrogen bonding between them when cracks were formed in the coating, and their strong wet adhesive properties also contribute to the regeneration of the coating

by generating other noncovalent interactions. We have attempted to introduce a drug delivery function into this self-healable antimicrobial coating. We have also applied this coating to a variety of medical devices and verified their versatility.

BM03.03.25
Diffusion Modeling for the Predication of Bacterial Patterning on Vascularized Polymers Kayla Marquis, Benjamin Chasse and <u>Caitlin Howell</u>; University of Maine, Orono, Maine, United States.

The creation of rationally designed and spatio-temporally controlled surfaces for cell culture is of great interest in the pursuit of the next generation of advanced biointerfaces. Here, we explore the use of COMSOL Multiphysics modeling to calculate the mass transport of antibiotic compounds through a bio-inspired vascularized polymer system, and use this model to predict the growth pattern of a bacterial biofilm on the surface of the polymer. The vascular system geometry, antibiotic concentration, and diffusion coefficients define the model, and are used in conjunction with known bacterial growth parameters such as minimum inhibitory concentration and critical time to determine the final arrangement of the biofilm on the surface. The theoretical models are then compared to an experimental validation. This approach may prove useful in applications such as compact methods for separation of bacterial multi-cultures based on antibiotic resistance or the creation of multiple spatially isolated colonies from a single culture sample for high-throughput testing.

BM03.03.26
Prediction of Surface Wettability of Fresh and Aged Graphite Surfaces from First-Principles Density Functional Theory Simulations <u>ChunYu Lu</u>, ChiaYun Lai, Mariam S. Mansouri, Tuza Olukan, Harry Apostoleris, Ibraheem Almansouri and Matteo Chiesa; Khalifa University, Abu Dhabi, United Arab Emirates.

Elucidating the surface wettability of graphite has increasing attracted much attention owning to its applications in several engineering fields, including the CMOS industry, energy storage technology and steel casting. However, despite the abundant information in literature, the underlying mechanism for the temporal surface property variations is still not fully elucidated yet, particularly the role played by water vapor. Prediction of the intrinsic surface wettability of graphite from first-principles density functional theory simulations offers an opportunity to clarify the overall evolution. In this study, by combining density functional theory (DFT)-predicted water contact angles and DFT-predicted AFM force-distance curves with experimental temporal observations, we provide conclusive evidence to demonstrate that water adsorption itself causes the graphite surface to be more hydrophobic. This finding helps to explain the variations of surface properties between fresh and aged graphite surfaces in ambient air. Moreover, in this study, we propose a methodology to predict the surface wettability at the nanoscale by linking the adhesive energy at the solid/liquid interface and cohesive energy at the liquid/liquid interface with the DFT AFM-predicted force of adhesion through the Young–Dupre equation.

BM03.03.27
Investigation on Micromechanical Behavior of Living Cell with FEM Simulation <u>Guanlin Tang</u>[1], Massimiliano Galluzzi[1], Yu-Lin Shen[2] and Florian J. Stadler[1]; [1]Shenzhen University, Shenzhen, China; [2]The University of New Mexico, Albuquerque, New Mexico, United States.

Atomic force microscopy (AFM) indentation is a powerful technique to characterize micromechanical properties of soft materials including living cells, such as detecting alterations of single cell rigidity correlated to pathophysiological conditions. However, the mechanical data obtained from deep indentation measurements can be problematic to interpret due to heterogeneity of a cell, nonlinearity of indentation contact, and constitutive relations of hyperelastic soft material. In this work, living MDA-MB-231 cells were indented by spherical probes, and the morphological and mechanical data obtained were adopted to build an accurate finite element model (FEM) for a parametric study. Living cells can be considered as complex multi-layered systems comprising membrane, cytoskeleton layers (actin, tubulin, intermediate filaments), nucleus, and internal organelles. Initially, a 2D-axisymmetric numerical model was constructed with the main purpose of understanding the effect of geometrical and mechanical properties of constitutive parts such as cell body, nucleus, and lamellipodium. Then, a 3D finite element model was constructed to simulate indentation events with an asymmetric misalignment geometry. Deformation field from FEM simulations were directly compared with atomic force spectroscopy to resolve the mechanical convolution of heterogeneous parts and quantify Young's modulus and geometry of nuclei. The results showed that nuclei of adherent MDA-MB-231 in standard conditions are 3-4 times stiffer than the surrounding cell body. 3D simulations demonstrated the nucleus shifting laterally during asymmetric indentation, underlining how a stiffer nucleus can prevent deformability (and therefore damage) caused by external force stimuli.

BM03.03.28
Preliminary Multiscale Studies of the Montmorillonite, Amylose, Fatty Acids and Water for Polymer-Clay Nanocomposite Modeling <u>Felipe A. Azevedo Rios Silva</u>[1, 3], Elaine R. Maia[1], Maria José A. Sales[1], Latifa Chebil[2] and Mohamed Ghoul[2]; [1]Instituto de Química, Universidade de Brasília, Brasilia, Brazil; [2]École Nationale Supérieure d'Agronomie et des Industries Alimentaires, Université de Lorraine, Vandœuvre lès Nancy, France; [3]Escola de Exatas, Arquitetura e Meio Ambiente, Universidade Católica de Brasília, Brasilia, Brazil.

More than ever, biodegradable polymers attracts much attention in polymer science.[1] Although, some biopolymers, such as starch, presents disadvantages such as poor processability.[2] In order to circumvent those disadvantages, researchers mix those polymers with compounds such as clays. This work presents the final part of a theoretical study of a Polymer-Clay Nanocomposite (PCN) composed by: starch, Pequi vegetable oil and montmorillonite (MMT), a phyllosilicate. In the present study, amilose oligomers, oleic, palmitic and stearic acids in the proportion found in the vegetable oil, montmorillonite and water, acting as solvent involved in the experimental medium,[2] were studied, as an simplified model, in order to simulate in multiscale their structural and behavioral correlations. The calculations were carried out by Molecular Mechanics, Dynamics (MM/MD) and Dissipative Particle Dynamics (DPD) methods at 363 K[3] and variable dynamic times, using Materials Studio™ software. In the dynamic trajectories, the organic molecules organized near the MMT, strongly interacting with it. The MD simulations were used as a basis to calculate the interaction parameters for the DPD model, which showed similar characteristics. The organic material concentrated near the MMT surfaces, what correlated with the MD results, implying in the validity of the model. The new knowledge acquired about those molecular systems, works as a starting point to build more complex models and, if the theoretical work converge with the experimental findings, will encourage further studies in the design of PCNs with biopolymers.
Acknowledgements: This work was supported by CNPq, CAPES, UnB and Université de Lorraine.
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BM03.03.29
Enhanced Icephobic Surface Using Porous Silica Particles Mi-jin Kim[1], Beom Jin Yoon[1], Jin Hwan Kim[1], Byungsu Lee[2], Daechul Kim[2] and <u>Youngseok Kim</u>[1]; [1]Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of); [2]Kangnam Jevisco Co., LTD., Gunpo, Korea

(the Republic of).

Icephobicity is usually defined as the ability to delay and prevent ice nucleation and formation on surfaces induced either by pouring a supercooled water. Formation, adhesion, and accumulation of ice, snow, frost, glaze, rime, or their mixtures can cause severe problems for solar panels, wind turbines, aircrafts, heat pumps, power lines, telecommunication equipment, and submarines. Recently, extremely low ice adhesion was introduced by tailoring the cross-link density of different elastomeric coatings and by enabling interfacial slippage of surface. But, the icephobicity for such surfaces can be short-lived, as the oil may be displaced and removed by water droplets or frost, or during accreted ice removal.
Here, we introduced oil-impregnated silica particles into modified hydrophobic polyurethane. The swelling capacity of oil was greatly increased by the porosity of particles, which promises durability of slippery surface. The roughness of particle-disperedd surface also enhanced hydrophobicity. The measured the interfacial friction force between the ice and the film agreed improved icephobicity with durability

BM03.03.30
Solvent Induced Coil-to-Globule Conformation Change of a Single Poly(acrylic acid) Chain <u>Yaxin An</u>, Karteek K. Bejagam and Sanket A. Deshmukh; Virginia Tech, Blacksburg, Virginia, United States.

Poly(acrylic acid) (PAA) is a polymer with carboxylic acid as pendant side-chains. The conformation of the PAA chains is sensitive to changes in the pH, salt concentration, and solvents, which makes it a good candidate as stimuli-responsive polymers. To investigate the effects of solvents on the structure of the PAA polymers at atomistic level, the all-atom (AA) PAA model was solvated in pure water, pure dimethylformamide (DMF), and mixtures of these two solvents of varying concentrations. Molecular dynamics (MD) simulations were performed to analyze the conformation of the PAA and the local solvent structure around the PAA chain. The radius of gyration (Rg) of the PAA chain in pure water and pure DMF were ~10.0 Å and ~14.0 Å at 300 K, representing its globule-like and coil-like state, respectively. The local structure of the solvents at the polymer-solvent interface was characterized by the radial distribution functions (RDFs) between polymer and solvents. The intra-molecular and inter-molecular hydrogen bonds of PAA, and the hydration free energy of the monomer of PAA in different solvents were calculated to probe the the polymer-polymer interaction and the polymer-solvent interaction. This study of the AA model of PAA paves the way for developing coarse-grained PAA models.

SESSION BM03.04: Multiscale Modeling of Soft Materials and Interfaces III
Session Chairs: Burkhard Duenweg and Meenakshi Dutt
Tuesday Morning, November 27, 2018
Sheraton, 2nd Floor, Back Bay B

8:00 AM BM03.04.01
Development of Transferable Coarse-Grained Models of Amino Acids <u>Olivia Conway</u>, Yaxin An, Karteek K. Bejagam and Sanket A. Deshmukh; Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia, United States.

Amino acids are important structural units of biomolecules and biomaterials such as peptides, proteins, and peptide amphiphiles (PAs). The focus of this study is on developing accurate transferable coarse-grained (CG) models of twenty standard amino acids. In CG models a group of a few or several atoms is represented by a bead, which can allow the modeling of processes like self-assembly of biomolecules and biomaterials. A 2:1 to 4:1 mapping scheme, where a CG bead is comprised of two to four heavy atoms and associated hydrogens, is employed to represent functional groups in amino acids. The amino acid backbone is comprised of two beads, while the side chains are comprised of one to five beads. The bonded parameters for the CG model are obtained from atomistic distributions of all-atom models of dipeptides. Nonbonded parameters are optimized using the particle swarm optimization (PSO) method to reproduce experimental properties (e.g. solvation free energy, surface tension, and density) of analogues of the side chains and backbone of the amino acids. In the near future, we plan to utilize these new CG models to construct PAs and simulate their self-assembly in the presence of explicit water models to elucidate the mechanism of their self-assembly. The knowledge gained from our study could then be used to aid the successful development of new PAs with potential applications in the field of drug delivery, regenerative medicine, tissue engineering, and stabilized photosynthetic complexes.

8:15 AM BM03.04.02
Modeling Surfactant Micellization with Solvent Accessible Surface Area <u>Hsieh Chen</u>[1] and Athanassios Z. Panagiotopoulos[2]; [1]Aramco Services Company: Aramco Research Center-Boston, Cambridge, Massachusetts, United States; [2]Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, United States.

We report a new implicit-solvent simulation model for studying the self-assembly of surfactants, which the hydrophobic interactions were captured by calculating the relative changes of the solvent accessible surface area (SASA) of the hydrophobic domains. Using histogram-reweighting grand canonical Monte Carlo simulations, we demonstrated that this approach allowed us to match both the experimental critical micelle concentrations (cmc) and micellar aggregation numbers simultaneously with a single phenomenological surface tension γ_{SASA} for the poly(oxyethylene) monoalkyl ether (C_mE_n) surfactants in aqueous solutions. Very good transferability was observed that the same model can accurately predict the experimental cmc and aggregation numbers for the C_mE_n surfactants with alkyl lengths m between 6 and 12, and poly(oxyethylene) lengths n between 1 and 9. The implicit-solvent model with SASA calculations put forward in this study is general and may be applied to study the more complex amphiphilic systems such as the surfactants with branched alkyl chains, or the surfactant and hydrocarbon mixtures.

8:30 AM BM03.04.03
Data-Driven Ultrafast Prediction of the Protein's Natural Frequency Spectrum by Machine Learning <u>Zhao Qin</u> and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Proteins are one of the basic biopolymers that can be generally found in many different forms in the body of living organisms. A protein molecule is usually composed of one or several polypeptide chains that combine to form a certain folded three-dimensional protein structure. The protein structures are easily excited by external force causing vibration or structural transition. One efficient way to extract the natural frequency of a protein is normal mode analysis (NMA), which provides the frequency and normal modes of the most general motion of a protein structure. However, NMA can be difficult for large protein structures since it will be both compute and memory intensive to solve the eigenvector and eigenvalue of the Hessian matrix, which is a square matrix composed of second-order partial derivatives of the potential energy function of all the constituting atoms of the protein structure. Here, we developed a machine-learning algorithm that allows us to efficiently compute the vibrational spectra of a protein without solving the hessian matrix nor

using any chemical force field. To build the algorithm, we wrote our own code to compute and build a database of the first 70 normal modes of over 100,000 protein structures available in the Protein Data Bank by using NMA in a consistent manner. We train our algorithm by randomly pick up 80,000 proteins out of the database (80%) and explore the correlation between their natural frequency and the other structural features of the protein (size and secondary structure content) that are easier to be measured with a convolutional neural network. We test the performance of the machine-learning model by predicting the natural frequency of the rest 20,000 protein structures (20% of the database) by giving their structural features. We find the predictions given by our algorithm can largely explain the natural frequency of these protein structures, especially for their low-frequency region (<20 cm-1). The correlation coefficient between the predicted frequency and the frequency given by NMA is over 0.9, demonstrating the reliability of this machine learning algorithm. This method will be useful to obtain the natural frequencies of protein structures without knowing their detailed atomic geometry, which may be helpful for the analysis of a frequency spectrum and the quick recognition of the unknown chemical molecules. Besides frequency prediction, we conclude the presentation with the demonstration of a new musical instrument, the EigenProt, that creates complex sounds based on the vibrations of more than a 100,000 protein structures.

8:45 AM BM03.04.04
Neural Coarse Graining for Molecular Dynamics Simulations <u>Wujie Wang</u> and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Molecular dynamics (MD) simulations provide key insights into the microscopic behavior of materials and, as a predictive tool, allow theory-driven design of functional materials. However, because of the large temporal and spatial scales involved in thermodynamic and kinetic phenomena in materials, atomistic simulations are often computationally infeasible. Coarse graining methods are widely used to tackle the challenge of expensive atomistic simulations. Current coarse graining methods require intensive manual tuning to determine both the coarse graining rules and the force field parametrization [1]. Inspired by recent works that achieve deep learning based accelerated calculation in Density Functional Theory [2], molecular kinetics [3] and free energy landscape calculations [4], we propose an alternative data-driven framework utilizing auto-encoders to map the atomistic trajectory into a latent space of coarse grained "super-atoms". By training on data from atomistic molecular dynamics trajectories or electronic structure calculations, this approach adopts stochastic gradient optimization of the coarse-graining rules, the force field parametrization and the up-resolution rules. Thus, it can provide parameters for large scale coarse-grained calculations and also map the coarse-grained trajectory back to dynamic information with atomistic details. Through this approach, systematic coarse graining pipelines can be built for fast molecular dynamics simulations and high-throughput predictions of the thermodynamics and kinetics of materials.

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9:00 AM BM03.04.05
A Hierarchal Approach to Understand Kevlar Using Quantum and Classical Molecular Dynamics <u>Subodh C. Tiwari</u>, Sungwook Hong, Paulo S. Branicio, Rajiv Kalia, Aiichiro Nakano and Priya Vashishta; Univ of Southern California, Los Angeles, California, United States.

The outstanding strength-to-weight ratio of para-aramid fibers, such as Kevlar and Twaron, can be largely attributed to their high content of p-phenylene terephthalamides (PPTA) crystals. Here, we perform non-adiabatic shock loading on large PPTA crystal models along different low-index crystallographic directions using quantum molecular-dynamics simulations. Results reveal an anisotropic shock response displaying elastic, plastic, and phase transformation from crystalline to para-crystalline configuration.
A reactive forcefield is developed and verified based on the shock data obtained using quantum molecular dynamics. Further, we performed reactive forcefield simulation to include the effect of chain end in PPTA. The simulation results provide an atomistic view on the shock absorbing mechanism during shock in para-aramid synthetic fibers.

9:15 AM BM03.04.06
Using Particle Swarm Optimization to Develop Lennard-Jones Parameters Between Hexagonal Boron Nitride and Water <u>Preeya F. Achari</u>, Karteek K. Bejagam and Sanket A. Deshmukh; Chemical Engineering, Virginia Tech, Blacksburg, Virginia, United States.

Hexagonal boron nitride (BN) has shown great potential in lubrication, electronic devices, sensors, and as an additive for cosmetic products due to its light weight, thermodynamic and chemical stability, great strength-to-weight ratio, and increased resistance to oxidation. Its used in microfluidic and nanofluidic applications at the molecular level demands accurate force-field parameters to describe the interactions between BN and water molecules. In this study, particle swarm optimization (PSO) and machine learning (ML) were coupled with molecular dynamics (MD) simulations to accelerate the development of Lennard-Jones (LJ) parameters, which are used to describe the non-bonded interactions between a water droplet and a sheet of hexagonal BN. Three commonly used water models, namely, SPC, SPC/Fw, and SPC/E were employed to describe water, while the BN sheet was modelled using REBO potential. The LJ parameters were optimized to reproduce the nanoscopic contact angle of water on the BN sheet.

9:30 AM *BM03.04.07
Coupling Lattice Boltzmann and Molecular Dynamics—A Versatile Tool for the Study of Soft-Matter Hydrodynamics <u>Burkhard Duenweg</u>[1, 2]; [1]Max Planck Institute for Polymer Research, Mainz, Germany; [2]Department of Chemical Engineering, Monash University, Melbourne, Victoria, Australia.

The talk outlines the methodology of Lattice Boltzmann (LB) simulations for hydrodyamics, and its stochastic version to include thermal fluctuations. To study colloidal dispersions, polymer solutions, and similar systems, a particle system is run by Molecular Dynamics, and coupled to the LB background by a Stokes friction force and a Langevin force. The method can be shown to represent both statistical mechanics and hydrodynamics fully consistently. A particularly successful application was the solution of the problem of hydrodynamic screening in semidilute polymer solutions. If time permits, the talk will also outline new (and so far not yet fully successful) attempts to base stochastic LB rigorously and approximation-free on the underlying Boltzmann entropy that governs the statistical mechanics of the system.

10:00 AM BREAK

10:30 AM BM03.04.08
State of Trapped Matter Inside Graphene Nanobubble Petr Zhilyaev, Evgeny Iakovlev and Iskander Akhatov; Skolkovo Institute of Science and Technology, Moscow, Russian Federation.

Graphene nanobubbles are formed when material is trapped between graphene and atomically flat substrate. Van der Waals interaction between graphene and the substrate results in the high pressures up to 1 GPa inside the grapahene nanobubble. Such extreme pressures and confinement could lead to phase transition in trapped material. Here we present multiscale model that describes both the state of matter inside the graphene nanobubble and its mechanical properties. Adhesion energies and their dependence on the thermodynamics parameters is calculated on atomstic level, energy is evaluated in continuum. We apply developed model to the graphene nanobubble on the graphite substrate with argon inside. Super critical state of argon is predicted at room temperature for graphene nanobubbles with radius in range from 100 to 500 nm. Gas phase of argon is emerged inside graphene nanoubbles with radius greater than 500 nm.

10:45 AM *BM03.04.09
Interfacial Effects on Free Volume, Mobility and Glassiness Jane Lipson, Ronald White and Jeffrey DeFelice; Dartmouth College, Hanover, New Hampshire, United States.

Finite homogeneous materials are contained by interfaces, whose influence on bulk properties is typically unremarkable. However, as the interfacial presence begins to dominate, for example in an ultrathin film or a sample loaded with nanoparticles, significant perturbations in behaviour may result. While it is evidently the material in very close proximity to an interface - e.g. within several nanometers - that is directly affected, the consequences can extend tens of nanometers into the sample. As a result, sample averaged properties might be significantly different from those of the bulk.
This talk will focus on links between changes in local mobility and free volume as interfaces are introduced, and how those changes translate into altering dynamic relaxation and the glass transition. We have recently shown that the Cooperative Free Volume (CFV) theory can resolve bulk dynamic relaxation data over a broad temperature and pressure range, including the span from Arrhenius to non-Arrhenius behaviour. Most recently, we have turned to studying thin films, and found intriguing connections between interfacial confinement and pressure. Application of CFV analysis to experimental dielectric relaxation data will be described, as well as prediction of trends.
The work discussed will also include simulation results using our simple Limited Mobility (LM) model. Here the focus will be on predicting interfacial effects caused by introducing additives into a bulk sample. The LM data reveal connections between the un/favourability of short-range polymer-additive interactions and sample-wide changes in glassiness and local mobility. The LM predictions show good agreement when tested both against experimental data and relative to results from more detailed simulation treatments.

11:15 AM *BM03.04.10
From Small to Large to Very Large—Multi-Scale Modeling of Biomolecular Structures in Implicit Solvent Alexey Onufriev; Virginia Tech, Blacksburg, Virginia, United States.

Water is as important to biomolecular simulations as it is to biology. However, accurate treatment of solvation effects explicitly, by representing solvent as discrete particles, can be computationally expensive. A popular alternative that can speed-up practical simulations is based on representing solvent as a continuum: solvent effects on the biomolecule in question are accounted for implicitly, at various levels of approximation. Molecular simulations within this so-called implicit solvent can speed up conformational search dramatically. Here I will discuss the foundations of the methodology and some of its new multi-scale variants. I will also discuss applications across many length scales: from atomistic simulations of the folding of small proteins to studies aimed at understanding chromatin compaction and dynamics at the level of the entire cell nucleus.

11:45 AM BM03.04.11
Understanding the Thermomechanical Response of Polymer Nanocomposites via Predictive Coarse-Grained Modeling Wenjie Xia; North Dakota State University, Fargo, North Dakota, United States.

Understanding and predicting the thermomechanical responses of polymer materials are challenging as their responses are greatly influenced by many factors, such as interfacial energy and filler volume fraction, giving rise to the presence of nanoscale interfaces. To overcome the spatiotemporal limitations of atomistic modeling, we have recently established an atomistically informed coarse-graining technique, called energy-renormalization approach, to achieve temperature transferability for coarse-grained (CG) modeling. Here, we employ our CG models to investigate how the nanoscale interface and free surface influence the mechanical and glass transition properties of polymer films and nanocomposites. Taking cellulose nanocrystal and poly(methyl-methacrylate) (PMMA) nanocomposites as a relevant model system, we present a multi-scale framework built upon our CG approach and machine learning algorithms to allow the prediction of thermomechanical properties of nanocomposite as a function of interfacial energy and filler volume fractions. Our established multi-scale framework is validated by recent experiments and breaks new ground in predicting key structure-property relationships for polymer nanomaterials.

SESSION BM03.05: Multiscale Modeling of Soft Materials and Interfaces IV
Session Chairs: Amanda Barnard and Sanket A. Deshmukh
Tuesday Afternoon, November 27, 2018
Sheraton, 2nd Floor, Back Bay B

1:30 PM *BM03.05.01
Nanostructure and Interfacial Characterisation Using Image Classification and Machine Learning Baichuan Sun and Amanda S. Barnard; CSIRO, Parkville, Victoria, Australia.

Restricting materials informatics to the numerical parameters output from conventional materials modelling software restricts us to a subset of machine learning methods capable of uncovering structure/property relationships and driving materials discovery and design. Presented here is a simple way of converting materials structures in to unique image-based fingerprints suitable for image processing methods that does not require subjective pre-assessment of the data and selection of descriptors by the user. This combination of methods is shown to classify the morphologies of in a meaningful way, and predict the correlation with the functional properties in agreement with other machine learning methods that required user intervention. This image-based, rather

than feature list-based, description of nanoparticle surfaces can be extended to more complex interfaces including macromolecules.

2:00 PM BM03.05.02

A Multiscale Model for Solute Diffusion in Hydrogels <u>Eneko Axpe</u>[1], Giovanni Offeddu[3], Yin Chang[4], Doreen Chan[2], David Merida[5] and Eric A. Appel[1]; [1]Materials Science and Engineering, Stanford University, Stanford, California, United States; [2]Chemistry, Stanford University, Stanford, California, United States; [3]Biological Engineering, Massachusetts Institute of Technology, Boston, Massachusetts, United States; [4]Engineering, University of Cambridge, Cambridge, United Kingdom; [5]Electricity and Electronics, University of the Basque Country, UPV/EHU, Bilbao, Spain.

Currently, solute diffusion in hydrogels is modeled by at least one of three main theories (hydrodynamics, free volume and obstruction theory), proceeding from distinct diffusion mechanisms. However, a comprehensive predictive model is lacking, so that time and capital intensive trial-and-error procedures are used to test the viability of hydrogel applications. In this presentation, a model for the diffusivity of solutes in hydrogels that combines the three main theories will be introduced. The model is verified by a combination of (i) positron annihilation lifetime spectroscopy (PALS) to measure the sub-nanoscopic free volume, (ii) instrumented indentation to quantify mesh size, and (iii) fluorescence recovery after photobleaching (FRAP) to quantify the diffusivity of dextran solutes of different sizes in poly(ethylene glycol) hydrogels with various mesh sizes. The model presented here outperforms traditional models.

2:15 PM BM03.05.03

Multiscale Modeling Framework with Application to the Facet Capsule Ligament and Podocytes <u>Jacob Merson</u>, Sai S. Deogekar, William R. Tobin, Catalin Picu and Mark S. Shephard; Rensselaer Polytechnic Institute, Troy, New York, United States.

A multiscale strategy is presented which is used to model various types of biological structures such as the cervical facet capsular ligament (FCL), and the podocyte; a cell responsible for filtration in the kidney. This strategy allows the micromechanical representation of the biological tissues as collagen networks, and the direct use of the detailed geometry obtained through various microscopy techniques.

In the FCL we start from the observation that the volume of the ligament is divided in a patchwork of sub-domains, each having a different direction of preferential fiber orientation. Such preferential orientation produces hydrostatic stress amplification and increased fluctuations. We construct a model based on the FCL geometry and perform a parametric study to determine the effect of the preferential orientation on the overall mechanical properties, and microscale fiber reorientation. This study is pertinent because the microscale fiber reorientation has been linked to FCL damage and pain. The multiscale method is also applied to study the deformation of podocytes due to capillary distention. This study is relevant for podocyte degeneration which is associated with degradation of renal function. We determine the threshold strain beyond which such degradation is expected.

2:30 PM *BM03.05.04

Rheology and Relaxation of Entangled Polymers in Strongly Nonlinear Extensional Flows Thomas C. O'Connor[1], Austin Hopkins[1], Nicolas Alvarez[2] and <u>Mark O. Robbins</u>[1]; [1]Johns Hopkins Univ, Baltimore, Maryland, United States; [2]Drexel University, Dept Chemical Engineering, Philadelphia, Pennsylvania, United States.

Nonlinear extensional flows are common in polymer processing but remain challenging theoretically because dramatic stretching of chains deforms the entanglement network far from equilibrium. Tube and slip-link models that describe flow of melts near equilibrium must be enriched to describe these states, but it is not clear what physics is missing. Here, we address this problem by performing coarse-grained simulations of extensional flows in entangled polymer melts for Rouse-Weissenberg numbers Wi=0.06-52 and Hencky strains >6. Simulations reproduce experimental trends in extensional viscosity with time, rate and molecular weight. Studies of molecular structure reveal an elongation and thinning of the confining tube with increasing Wi. The rising stress is quantitatively consistent with the decreasing entropy of chains at the equilibrium entanglement length. Molecular weight dependent trends in viscosity are related to a crossover from the Newtonian limit to a high rate limit that scales differently with chain length. Stress relaxations from steady state reveal chains rapidly retract and recover their equilibrium tube diameter even when chain primitive paths are fully aligned and do not intersect. Contrary to some geometric models of entanglement, our results suggest the degree of chain confinement is independent of the orientation of the entanglement network. The results are used to test and constrain generalizations of tube and slip-link models to strongly nonlinear flows.

3:00 PM BREAK

3:30 PM BM03.05.05

Integral Equation Coarse-Graining Simulation Approaches for the Mixtures of Polymer Melts—Composition-Dependent Effective Potentials <u>Mohammadhasan Dinpajooh</u> and Marina Guenza; University of Oregon, Eugene, Oregon, United States.

Mixtures of polymers with different compositions are of great importance for many technological and industrial applications because as the composition of polymers change, the mixture structure and dynamics can change significantly. Molecular simulations may be used to study polymer mixtures but their properties develop on such an extended range of time and length-scale that they cannot be investigated by atomistic simulations. In this regard, the integral equation coarse-graining (IECG) approach has been developed in which the polymers are either represented as soft spheres or multi coarse-graining (CG) sites, where each CG site consists of a large enough number of monomers to use Gaussian statistics to obtain the intramolecular correlations. The IECG method is based on the liquid state theory and solves the Ornstein-Zernike equation to obtain the intermolecular correlations, and consequently the effective CG potentials. Representing polymer melts with a given degree of polymerization at various resolutions, we use the IECG theory and/or perform the IECG simulations to investigate the properties of the same polymer melt represented by mixtures of CG models at various resolutions. We show that the structural and thermodynamical properties, such as pressure and pair correlation functions, for such mixtures are consistent with pure CG liquids as well as the underlying atomistic simulations. We also address the compositional dependence of the effective IECG potential, along with its range for various types of mixtures.

3:45 PM BM03.05.06

Replica Exchange Enhanced Self Assembly of Ultrashort Peptides <u>Srinivas Mushnoori</u>[2], Vivek Balasubramanian[1], Doaa Altarawy[4], Benjamin Pritchard[4], Shantenu Jha[3] and Meenakshi Dutt[2]; [1]Electrical and Computer Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; [2]Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; [3]Electrical and Computer ENgineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; [4]Molecular Sciences Software Institute, Virginia Tech, Blacksburg, Virginia, United States.

Replica-Exchange (RE) is a class of simulation techniques used to enhance sampling and comprehensively explore phase space of simulations. Originally proposed using Monte Carlo methods, RE techniques have since found their way into Molecular Dynamics (MD) methods, particularly for addressing problems of large, complex biomolecular systems. RE simulations are generally used for exploring single proteins or peptides, but seldom to explore

assembly. Assembly of biomolecules constitutes a class of physical processes which are especially susceptible to kinetic traps. RE provides enhanced sampling that aids the systems in overcoming these kinetic traps. In this study, we apply the REMD technique to the assembly of ultrashort peptides and explore the morphological diversity of the supramolecular structures.

4:00 PM BM03.05.07
Bridging Time Scales with Variationally Enhanced Sampling Omar Valsson; Max Planck Institute for Polymer Research, Mainz, Germany.

The usefulness of atomistic simulations is generally hampered by the presence of several metastable states separated by high barriers leading to kinetic bottlenecks. Transitions between metastable states thus occur on much longer time scales than one can simulate. Numerous enhanced sampling methods have been introduced to alleviate this time scale problem, including methods based on identifying a few crucial order parameters corresponding to the relevant slow degrees of freedom and enhancing their sampling through the introduction of an external biasing potential [1].

Here we will discuss Variationally Enhanced Sampling [2], a generally applicable enhanced sampling method where an external bias potential is constructed by minimizing a convex functional. We present numerous examples from physics, chemistry, and materials science which show the flexibility and practicality of the method [3-6]. We will furthermore show how the variational property of the method can be used to extend the method in various innovative ways, e.g.: to obtain kinetic information from atomistic simulation [7]; to accelerate nucleation events by employing models from classical nucleation theory [8]; to parameterize coarse-grained phenomenological models from microscopic simulations [9]; and to incorporate experimental information into molecular simulations.

We will also introduce the VES code [10], an open-source library for the PLUMED 2 plugin that implements methods based on Variationally Enhanced Sampling.

Literature:

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4:15 PM BM03.05.08
Hiking on the Energy Landscape—All-Atom Computational Understanding of the Universality of Long Timescale Phenomena and Rare Events in Non-Equilibrium Matter—Metal, Water and Protein Yang Zhang; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

In the last few years, we have developed an all-atom metadynamics method, which allows intelligently sampling statistically rare events in complex materials, and a Relaxation-Excitation Mode Analysis (REMA) theoretical framework, which links the computationally sampled statistics of the energy landscape to experimentally measurable two-point correlation functions. This synergistically integrated experimental and computational approach opened the way for qualitatively examining a range of non-equilibrium matter and the associated complex processes that occur over a very long timescale, such as the viscous flow of supercooled liquids and glasses, nucleation and crystal growth, the folding of polypeptide chains into structured proteins, the self-assembly of micro-units into functional objects, and aging and degradation of materials. In this talk, first I will show the intriguing energy landscape characteristics of three apparently-different systems: glass-forming metallic liquids, water, and protein; then, I will describe our quantitative investigations of how confinement blocks the transition pathways on the energy landscape of proteins and thus prevents their thermal unfolding/denaturation.

4:30 PM BM03.05.09
Multiscale Modeling of Fibrils in Bone—Bridging Collagen-Mineral Interaction to Macroscale Properties Dinesh R. Katti and Kalpana Katti; North Dakota State University, Fargo, North Dakota, United States.

Bone is an essential biological nanocomposite found in the human body that plays a vital role in providing structural integrity and mobility to the human body. Bone displays structural hierarchy spanning from the molecular scale to the macroscale, beginning with well-organized arrays of collagen molecules and nanoscale hydroxyapatite which in turn form the fibrils followed by concentric lamella and the osteon and finally the macroscopic bone. The role of molecular interactions between the nanosized hydroxyapatite and collagen on the mechanics of collagen is evaluated using molecular dynamics simulations. In addition, detailed steered molecular dynamics studies on the mechanics of full length collagen of 300nm size, are conducted and the impact of inter-chain molecular interactions on the structure of collagen and mechanics on the collagen are mechanistically evaluated. The mechanical response obtained from molecular scale studies are incorporated into a 3D finite element model of fibril using a hierarchical multiscale modeling approach. Simulations using the finite element models of collagen fibril are conducted to study the elastic and inelastic response of the fibril. These simulations provide an insight into key mechanisms that influence the mechanics of fibril and indicate that the molecular scale interactions at collagen-mineral interfaces have a significant impact on the mechanics of the fibril. Further, we report the role of crosslink densities in collagen fibrils on the mechanics of the fibril. These studies are vital towards understanding ageing and diseases in bone.

4:45 PM BM03.05.10
Structural Evolution in Polymer Nanocomposite Fibers—A Molecular Dynamics Simulation Approach Sojeong Heo[1], Jeong-Eun Lee[1], Seunggeol Lee[2] and Han Gi Chae[1]; [1]UNIST, Ulsan, Korea (the Republic of); [2]Pusan National University, Busan, Korea (the Republic of).

Carbon nanotube (CNT)-based polymer nanocomposites have often been processed into fibers because fibrous shapes are one of the best methods of fully exploiting the anisotropies and structures of CNTs. Among various types of polymer-CNT nanocomposite fiber, polyacrylonitrile (PAN) has been among the most studied polymeric system because it strongly interacts with CNTs and is the most common source of high-performance carbon fibers. In order to understand the structural evolution and related mechanical properties under extensional flow, molecular dynamics (MD) simulations were performed on polyacrylonitrile–single-wall carbon nanotube (PAN-SWNT) nanocomposites, to a draw ratio of two, which mimics fiber-spinning and drawing processes. Two $SWNT_{(5,5)}$- and $SWNT_{(10,10)}$-containing nanocomposite systems, as well as a control PAN, were constructed. Higher stresses were observed in both nanocomposite systems. In addition, higher Young's (4.76 GPa) and bulk (4.09 GPa) moduli were observed when the smaller-diameter $SWNT_{(5,5)}$ was

used, compared to those of PAN-SWNT$_{(10,10)}$ (4.41 GPa and 3.96 GPa, respectively), suggesting that SWNT$_{(5,5)}$ resists stress better. Furthermore, we also observed the formation of void structures at both ends of the SWNTs, especially for the large-diameter SWNT$_{(10,10)}$; these voids became larger in the drawing direction with increasing draw ratio and may adversely affect the mechanical properties of the nanocomposite fibers.

SESSION BM03.06: Multiscale Modeling of Soft Materials and Interfaces V
Session Chairs: Meenakshi Dutt and Roland Winkler
Wednesday Morning, November 28, 2018
Sheraton, 2nd Floor, Back Bay B

8:00 AM BM03.06.01
Uptake in Microspheres from Crystalline Nanocellulose—Modelling Diffusion and Kinetics Junqi Wu and Mark P. Andrews; Department of Chemistry, McGill University, Montreal, Quebec, Canada.

Crystalline nanocellulose(CNC) is a crystalline rod-like particle, derived from sustainable forests and biomass. CNC has emerged as a leading "platform" material with potential for broad spectrum applications in technology, including microspheres for intelligent drug delivery and microreactors. In the present work, CNC nano-rods are kinetically assembled into microspheres by spray drying. The transport properties of these micro-objects are investigated by measuring methylene blue dye uptake. Methylene blue dye adsorption kinetics are predicted using both pseudo-first, pseudo- second kinetics and film-pore diffusion models. The film-pore diffusion model equations were solved numerically by the method of lines, and the initial estimates of external-film transfer coefficients were obtained using single resistance models. Dye uptake Isotherms were investigated for large range of initial concentrations (from 5mg/L to 100mg/L) and isotherm type (Langmuir, Freundlich, and Temkin). The thermodynamics of dye adsorption were evaluated based on the kinetic data at different temperatures. The Gibbs free energy was estimated using both chemisorption kinetic models and diffusion kinetic models. Knowledge of CNC dye adsorption mechanisms and uptake is important to extract microstructural information of CNC microspheres. This can be used to further understand how small molecules can be delivered in and out of the micro-particles, and therefore to provide insight into how to control small molecule delivery using CNC micro-vehicles.

8:15 AM BM03.06.02
Bridging Scales of Diverse and Complex Crystal Structures from Atoms to Colloids Julia Dshemuchadse[1], Michael Engel[1, 4], Pablo F. Damasceno[2, 5], Carolyn L. Phillips[6], Matthew Spellings[1] and Sharon C. Glotzer[1, 2, 3]; [1]Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States; [2]Applied Physics Department, University of Michigan, Ann Arbor, Michigan, United States; [3]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States; [4]Department of Chemical and Biological Engineering, Friedrich-Alexander-University Erlangen-Nuremberg, Erlangen, Germany; [5]Department of Cellular and Molecular Pharmacology, University of California, San Francisco, California, United States; [6]Argonne National Laboratory, Argonne, Illinois, United States.

Soft condensed matter research has led to the discovery of increasingly intricate crystal structures over the last 15 years: systems of dendrimer or block copolymer micelles, colloids, and polymer- or DNA-grafted nanoparticles are found to crystallize in structure types that are known from atomistic compounds (*e.g.*, [1–5]). Examples for these crystal structure types are Laves phases (*e.g.*,cF24-MgCu$_2$, hP12-MgZn$_2$), Frank-Kasper phases and quasicrystal approximants (*e.g.*,cP8-Cr$_3$Si, tP30-CrFe), or clathrates (*e.g.*, cP54-K$_4$Si$_{23}$). Some of these building blocks can be tuned smoothly and span entire phase diagrams of structural behavior that can be likened to that of a multicomponent atomic system [6].

In this study, we simulate the self-assembly of one- and two-component systems of attractive particles that interact *via* short-ranged, isotropic pair potentials. Previous exploratory work had found these simple systems to be capable of forming highly complex structures, such as an icosahedral quasicrystal [7]. Here, we inspect large areas in such parameter spaces and find a variety of crystal structures with varying degrees of complexity, including structures with ultra-large unit cells. We systematically screen two phase spaces of one-component systems, and we explore the higher-dimensional design spaces of the two-component systems by incorporating machine-learning methods into our simulation scheme.

Although our model is short-ranged and fairly simple, we observe many geometric equivalents to atomic-scale structures. The continuous variation of the simulated interaction potentials results in a breadth of structures that spans the entire range of chemical interactions, from low-coordinated, covalent-like environments to highly-coordinated, metallic-like dense sphere packings. Our agnostic phase space exploration grants us a design flexibility beyond that of the periodic table and allows us to engineer new crystal structures to be synthesized in the future under exotic growth conditions or on the mesoscale.

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8:30 AM BM03.06.03
Interface-Mediated Assembly of Nanoparticles into Anisotropic Structures Tsung-Yeh Tang[1] and Gaurav Arya[2]; [1]Materials Science and Engineering, University of California, San Diego, La Jolla, California, United States; [2]Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States.

A significant challenge in the bottom-up fabrication of nanomaterials is assembling spherical or near-spherical nanoparticles into anisotropic architectures. One promising strategy is to use the interfacial tension between two immiscible solvents to trap particles at the interface; however, this approach is typically limited to producing two-dimensional assemblies. Here we demonstrate through molecular dynamics simulations that the interfacial tension across two immiscible polymers combined with the grafting of nanoparticles with polymer chains can be used to assemble spherical nanoparticles into unique anisotropic clusters, such as dimers with a tunable tilt angle at the interface, and more complex three-dimensional architectures, such as chiral ribbons with tunable curvature. We show that this approach can also be used to tune the orientation, and subsequent assembly, of shaped nanoparticles at the interface. Our results suggest that such interfacial assembly of nanoparticles could be a promising approach for fabricating next-generation polymer nanocomposites, where precise spatial and orientational organization of nanoparticles is required for proper function.

8:45 AM BM03.06.04

Multiscale Modeling of Polymer-Colloid Interactions in Waterbased Coatings Alyssa Travitz[1], Wenlin Zhang[2] and Ronald G. Larson[2]; [1]Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States; [2]Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Formulations containing rheology-modifying polymers and nanometer-sized colloids have widespread use in pharmaceuticals, personal care products, and water-borne coatings. A typical rheology-modifying polymer consists of a hydrophilic backbone with hydrophobic ends that associate with the hydrophobic surface of the colloids. These hydrophobic interactions drive the polymer to form either a loop on a single colloid or a bridge between adjacent colloids. The continual breakage and formation of loops and bridges results in a transient network with relaxation times that span several orders of magnitude. Because it is computationally infeasible to capture the full range of relaxation times while maintaining atomistic resolution, our group has developed a highly efficient hybrid population balance-Brownian dynamics model (Pop-BD). The Pop-BD model reduces the system to pairwise colloidal interactions with attractive contributions from bridging and repulsive contributions from the layer of loops on the colloid's surface. Currently, the Pop-BD model approximates the interactions between polymer-coated colloids as a steep, short-range repulsion. However, experimental data suggest that the layer of polymer loops is often a brush with much longer-range interactions. In this work, we use molecular dynamics simulations to study pairwise interactions of polymer-coated colloids with experimentally relevant coverage fractions. We compare the polymer density profiles from these simulations with small angle neutron scattering data and analytical calculations. Our results are in good agreement with self-consistent field theory and show repulsive potentials with ranges several times longer than previously assumed. In future studies, these repulsive pair potentials will allow us to study equilibrium phase behavior as well as to inform current models that capture the dynamics of these transient networks to ultimately predict and design the rheology of such systems.

9:00 AM BM03.06.05

Inverse Design of Pressure-Induced Solid—Solid Transitions in Colloids Using the Alchemical Ensemble Chrisy Xiyu Du[1, 2], Greg v. Anders[1], Julia Dshemuchadse[1], Paul Dodd[1] and Sharon C. Glotzer[1]; [1]University of Michigan, Ann Arbor, Michigan, United States; [2]School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

Recent developments in anisotropic particle synthesis have shown promise for using these particles as building blocks for functional materials. However, due to the large design spaces that are available to us, it can be challenging to find appropriate building blocks for target behaviors. Here, instead of mapping out the phase behavior for a range of particle shapes, we present a new, alternative computational statistical mechanical approach that couples together multiple systems within the "alchemical ensemble"—a generalized, statistical mechanical framework in which model attributes are allowed to fluctuate along with thermodynamic variables. The alchemical ensemble has application to a wide variety of design problems within statistical mechanics and this modeling and simulation approach bridges multiple scales by linking bulk properties to molecular simulations through design. Here, we demonstrate its use in the design of particle shapes for target materials properties, and present examples of candidate colloidal-and nano-particles designed within the alchemical ensemble specifically for structurally reconfigurable colloidal crystals.

9:15 AM BM03.06.06

Twisted Domains Get Edgy—Microrafts in Colloidal Membranes of Length-Asymmetric Rod Mixtures Douglas M. Hall[1], Joia Miller[3], Johanna Robaszewski[3], Prerna Sharma[4], Michael Hagan[3], Zvonimir Dogic[2, 3] and Gregory M. Grason[1]; [1]Polymer Science and Engineering, Univ of Massachusetts-Amherst, Amherst, Massachusetts, United States; [2]Physics, University of California, Santa Barbara, Santa Barbara, California, United States; [3]Physics, Brandeis University, Waltham, Massachusetts, United States; [4]Physics, Indian Institute of Science, Bangalore, India.

Osmotically-condensed colloidal membranes of rod-like, chiral filaments offer an experimental platform for directly probing intra-membrane microstructure formation processes that would be far more difficult, if not impossible, to observe at the nanometer scales of phospholipid membranes. In particular, membranes formed by two component mixtures of rods (either wild-type or mutant *fd*-virus particles) exhibit a remarkably rich set of intra-domain phase-separated morphologies, most notably the formation of raft domains whose lateral dimensions are self-limiting in equilibrium yet much larger than the range of rod-rod interactions. The prevailing theoretical model to explain this phenomenon focuses on the asymmetry in the *chirality*—a distinct preference for right- vs. left-handed intra-membrane twist for different species—as the stabilizing factor in raft formation. Notwithstanding its successes to capture the raft formation at a qualitative level, several recent experimental observations are not captured by this chirality-driven phase separation (CDPS) model. In particular, the degree of raft twist is shown to be a non-monotonic function of its radius, and there is a pronounced asymmetric behavior of rafts of tall vs. small rods, independent of their chirality. Small rods in background membrane of tall rods form finite size, twisted rafts. In contrast, tall rod domains in a background membrane of short rounds refuse to twist at their outer edge, and instead, become unstable to invaginated or annular morphologies that enclose stable, twisted small-rod rafts.

To understand these observations with develop a model to predict the microstructure and thermodynamic effects of the intra-rod domain edge. We show that geometrical constraints imposed by the twisting of straight (rigid) rods require splay of the mid-plane of the raft that has important consequences for the shape of the inter-domain edge. Our model predicts the existence of a thermodynamic coupling between domain edge curvature and rod-tilt through the dependence of membrane excluded volume to the 3D geometry of rod packing. We show that the thermodynamics of this this curvature/tilt coupling not only captures the asymmetric dependence of raft behavior on their height (i.e. tilted domain edges generically favor bending *towards the shorter rod domain*) their effects are quite distinct from the CDPS model (i.e. they lead to free energy terms that are *achiral* and proportion to domain edge curvature). We argue further, based on symmetry principles, that this curvature/tilt coupling is generic, and as such should exist *in any model of phase-separating membranes* as a coupling between in-plane tilt and second-derivatives of (scalar) composition.

9:30 AM *BM03.06.07

Clustering and Collective Dyanmics of Microswimmers—Effects of Shape and Hydrodynamics Roland G. Winkler and Gerhard Gompper; Institute for Advanced Simulation, Forschungszentrum Jülich GmbH, Jülich, Germany.

Structure formation of active colloidal particles is governed by their shape and hydrodynamic interactions [1], but the effective dimensionality of the system, i.e., three-dimensional bulk fluid versus thin film, plays also a major role. In order to address these various aspects, we have studied structure formation of active dry and wet colloidal systems. Dry matter is modeled by active Brownian particles (ABPs), whereas in the presence of fluid, the active agent is described by a recently developed spheroidal squirmer [2]. The fluid is explicitly modeled by the multiparticle collision dynamics (MPC) approach, a mesoscale hydrodynamic simulation technique [3].

We have studied the swimming behavior, cooperative motion, and motility-induced phase separation (MIPS) of spheroidal squirmers in a narrow slit. For two squirmers, we find a strong influence of confinement on their cooperative motion caused by surface hydrodynamic interactions [2]. Considering the phase behavior of many squirmers, we find that hydrodynamic interactions suppress MIPS for spherical squirmers, but motility-induced clustering (MIC) is

present. This is in agreement with results in strictly two-dimensional systems [4], but disagrees with other simulation results for slits [5]. In contrast, hydrodynamic interactions enhance MIPS for elongated squirmers. Moreover, the swimmer type, characterized by the hydrodynamic multipole expansion of its flow field, i.e., puller, pusher, and neutral squirmer, strongly affects the phase behavior. A negative active-stress parameter (puller) is advantageous for MIPS, while a positive value (pusher) is disadvantageous.

The observed clustering of spheroidal squirmers is in contrast to the behavior of motile bacteria, e.g., *E. coli*, in suspensions, which display active turbulence [6]. At the moment, there is no detailed understanding of the different behavior and the underlying mechanisms. Possible hydrodynamic mechanisms will be discussed in the presentation.

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10:00 AM BREAK

10:30 AM BM03.06.08
Pressure-Tunable Photonic Band Gaps in an Entropic Crystal Rose Cersonsky, Julia Dshemuchadse, James Antonaglia, Greg v. Anders and Sharon C. Glotzer; University of Michigan, Ann Arbor, Michigan, United States.

Materials adopting the diamond structure possess useful properties in atomic and colloidal systems and are a popular target for synthesis in colloids where a photonic band gap is possible. The desirable photonic properties of the diamond structure pose an interesting opportunity for reconfigurable matter: can we create a crystal able to switch reversibly to and from the diamond structure with a photonic band gap in the visible light range? Drawing inspiration from high-pressure transitions of diamond-forming atomic systems, we design a system of polyhedrally-shaped colloidal particles that transitions from diamond to a tetragonal diamond derivative upon a small pressure change. The transition can alternatively be triggered by changing the shape of the particle *in-situ*. Additionally, our modeling and simulation approach bridges multiple length-scales by linking bulk property calculations to molecular simulations. We propose that the transition provides a reversible reconfiguration process for a potential new colloidal material and draw parallels between this transition and phase behavior of the atomic transitions from which we take inspiration.

10:45 AM BM03.06.09
Structure-Property Relationships of the Crystal-Amorphous Interface During Deformation of High-Density Polyethylene by Molecular Dynamics Simulations Andrew L. Bowman[1, 2], Sungkwang Mun[2], Steven Gwaltney[3], Mei Chandler[4], Michael Baskes[5] and M F. Horstemeyer[1, 2]; [1]Mechanical Engineering, Mississippi State University, Mississippi State, Mississippi, United States; [2]Center for Advanced Vehicular Systems (CAVS), Mississippi State University, Mississippi State, Mississippi, United States; [3]Chemistry, Mississippi State University, Mississippi State, Mississippi, United States; [4]U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi, United States; [5]Aerospace Engineering, Mississippi State University, Mississippi State, Mississippi, United States.

Molecular Dynamic (MD) simulations using a Modified Embedded Atom Method (MEAM) for saturated hydrocarbons is used to investigate the complex crystal-amorphous interface of High-Density Polyethylene (HDPE) at various applied strain rates (1e7 – 1e9) and stress states (tension and shear). A random walk algorithm is developed to model the crystalline-amorphous interface through the insertion of four types of amorphous chains within a crystalline domain: 1) tie chains connecting separate crystalline surface, 2) loop chains connecting separate points on the same crystalline surface, 3) chains originating from a crystalline domain and terminating within the amorphous region, 4) chains both originating and terminating within the amorphous region. To better understand the complex structure-property relations of the various polymer chains emanating and terminating within the crystalline and amorphous domains, a Design of Experiments (DOE) methodology is implemented to independently investigate the influence of eight parameters (number and length of each of the four chain types) concerning the crystalline-amorphous interface in uniaxial tension and simple shear boundary conditions. The relative volume fractions of amorphous to crystalline regions are studied in order to bridge the stress-strain behavior of a completely amorphous polymer and a completely crystalline polymer system. The addition of a small number of amorphous segments is shown to drastically lower the ultimate stress of the idealized completely crystalline material by acting as defects with the crystalline structure; a finding supported by theoretical and experimental observations. The findings of this study provide insights into the complex behavior of semi-crystalline polymers and provides a computational tool for the further investigation of the crystal-amorphous interface under more mechanically and chemically complex boundary conditions.

11:00 AM BM03.06.10
A Theoretical Model for Raft Interactions in Ternary Colloidal Membranes Chaitanya Joshi[1], Joia Miller[1], Douglas M. Hall[2], Arvind Baskaran[1], Gregory M. Grason[2], Zvonimir Dogic[3], Michael Hagan[1] and Aparna Baskaran[1]; [1]Brandeis University, Waltham, Massachusetts, United States; [2]University of Massachusetts, Amherst, Massachusetts, United States; [3]University of California, Santa Barbara, California, United States.

Colloidal membranes are a recently developed experimental system of rod-like chiral particles that self-assemble into one rod-length-thick mono-layers under the influence of a tunable depletion interaction. Despite being monolayers that are 1 micron thick, colloidal membranes are described by the same continuum theory as lipid bilayers, and their colloidal scale enables study of behaviors that cannot be visualized in lipid bilayers. Forming membranes from a mixture of short right-handed rods and long left-handed rods results in a rich phase behavior, including microphase separation, wherein one species forms finite-sized domains, or rafts, floating in a background of the other species. This talk will discuss the theoretical analysis of colloidal membranes comprised of three rod species: one with a shorter length and right-handed chirality, the other two with longer lengths and respectively right- and left-handed chirality. Controlling the composition of right-and left-handed long rods allows tuning the chirality of the background. Experiments have shown that making the long rod mixture effectively achiral leads to complex, non-pairwise interactions between the short-rod rafts. We employ a Ginzburg-Landau description of the system to understand how this behavior arises from a combination of chirality, rod length mismatches, and the depletion interactions. In particular, we find that raft interactions and their non-pairwise-additivity can be explained from the deformations of the background membrane. We also theoretically examine the experimental observation that there is an asymmetry between rafts of short rods in a background of long rods, or rafts of long rods in a short rod background --- the two systems lead to very different ensembles of raft morphologies.

11:15 AM BM03.06.11
Computational Design of Multi-Component Superstructures with Multi-Element Colloidal Building Blocks Using a Genetic Algorithm-Based Framework Mehdi Zanjani[1] and Dhananjai Rao[2]; [1]Mechanical and Manufacturing Engineering, Miami University, Oxford, Ohio, United States; [2]Computer Science and Software Engineering, Miami University, Oxford, Ohio, United States.

Engineering micro/nanoscale structures and interfaces through self-assembly of colloidal particles is a powerful approach in material design and processing. Colloidal building blocks, with a variety of shapes, sizes, and compositions, can self-assemble into different structures with desirable electronic, photonic, and phononic properties. Recent advances in synthesis and characterization of complex colloidal units, such as colloidal clusters and patchy particles, has provided a library of multi-element building blocks that can significantly expand the current scope of metamaterial self-assembly. However, the complexity of these building blocks makes it significantly harder to predict the resulting structures and their transport properties. Therefore, developing predictive tools based on computational and machine learning approaches becomes a necessity for successful implementation of new material design procedures with multi-element colloidal units.

In this study, we establish a computational framework to help identify feasible multi-component supercrystals of multi-element colloidal building blocks. Specifically, we investigate various designs for multi-component crystalline structures of four or more elements and map out feasible supercrystal phases. We also develop a computational framework to predict transport properties of the target multi-component supercrystals. Band structure calculations are performed to capture the influence of key parameters such as structural features and building block size/shape on the photonic and phononic properties of various proposed metamaterial designs. Finally, we present a Genetic Algorithm (GA) that is established based on the computational analysis of structural and transport features of the multi-component supercrystals. This GA uses Machine Learning techniques to define *material design rules* with respect to structure and transport properties of the desired multi-component supercrystals.

11:30 AM *BM03.06.12
Multi-Functional Active Sheets—Crawlers, Wrappers and Flappers Abhrajit Laskar, Oleg Shklyaev and <u>Anna C. Balazs</u>; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

We develop a computational model to describe the behavior of active, flexible sheets in solution that can undergo spontaneous self-sustained motion. The active sheets are uniformly coated with a catalyst that decomposes the reagent in the surrounding fluid. The resulting variations in the fluid density give rise to a convective flow around the catalyst-coated sheets. The chemically-generated fluid flow, in turn, dynamically "sculpts" the shape of the sheet and thereby enables it to perform a range of functions. For example, with a periodic influx of reagent, an initially flat, rectangular sheet undergoes repeated shape transformations and thereby exhibits directed crawling along the wall. We also consider a petal-shaped sheet that is anchored to the surface of the solution-filled microchamber. When all four petals are coated with the same catalyst, the generated flow propels the petals to bend and unbend, allowing the sheet to wrap and unwrap a particle localized on its surface. Finally, we examine how four-petal sheets that are coated with different catalysts, and thereby respond to different reagents, can be used to construct logic gates. The findings provide guidelines for creating autonomously moving active fabrics that can be made to crawl, envelop particles in solution or perform simple logic operations in a microfluidic device.

SESSION BM03.07: Multiscale Modeling of Soft Materials and Interfaces VI
Session Chairs: Alexander Alexeev and Jessica Nash
Wednesday Afternoon, November 28, 2018
Sheraton, 2nd Floor, Back Bay B

1:30 PM *BM03.07.01
Design of Nanomaterials for Gene Delivery Using Molecular Modeling Matthew D. Manning, Jessica Nash, Abhishek Singh and <u>Yaroslava G. Yingling</u>; North Carolina State University, Raleigh, North Carolina, United States.

The design of ligand functionalized inorganic nanoparticles (NPs) that can induce specific structural transitions in nucleic acids (NA) is important for nanotechnology applications including gene delivery and nanoelectronics. However, comprehensive understanding of ligand design principles lies in the cost associated with synthesizing and characterizing diverse ligand chemistries and ability to carefully assess the structural integrity of biomolecules upon interactions with NPs. It is known that the interaction of nucleic acids and nanoparticles may be tuned through changes in nanoparticle size, charge, polarity, or shape. However, the factors that affect structural transitions are not fully understood. We performed atomistic molecular dynamics simulations of the binding of nucleic acids to monolayer-protected gold nanoparticles to elucidate structural changes that take place for nanoparticles and DNA upon binding. Results from these simulations were analyzed to determine modes of DNA and RNA bending with nanoparticles. Our simulations show that highly charged nanoparticles cause DNA to bend with little damage to the helix structure, similar to DNA in the nucleosome. Nanoparticle shape as well as charge is shown to affect the wrapping of nucleic acids with the nanoparticle. Low salt concentrations and high nanoparticle charge cause greater disruptions to DNA structure. We find that the roll parameter is the most important base-pair parameter for DNA bending. Requirements for bending differed significantly between DNA and dsRNA. The degree of DNA bending is controlled by the charge of the NPs, but ligand flexibility played a more significant role in dsRNA bending. These results allowed us to determine the training data for machine learning algorithms and design a novel ligands capable of controlled wrapping of NA around NP. We have shown that the designer gold NPs are capable of wrapping NAs with fine control of binding strength through NP charge and ligand stiffness. These findings are useful for designing gene delivery systems with enhanced biocompatibility and selectivity.

2:00 PM *BM03.07.02
The Multi-Facetted Nature of Nanocrystal Growth Revealed by Multi-Scale Simulations <u>Kristen A. Fichthorn</u>; The Pennsylvania State University, University Park, Pennsylvania, United States.

Achieving the controlled synthesis of colloidal nanomaterials with selected shapes and sizes is an important goal for a variety of applications that can exploit their unique properties (e.g., optical, catalytic, magnetic, etc.). In the past decade, a number of promising solution-phase synthesis techniques have been developed to fabricate various nanostructures. A deep, fundamental understanding of the phenomena that promote selective growth and assembly in these syntheses would enable tight control of nanostructure morphologies in next-generation techniques. I will present several aspects of our efforts to understand how shape-selective growth occurs in these syntheses.

First, I will discuss how PVP, a structure-directing polymer, facilitates the formation of {100}-faceted Ag nanocubes. In these studies, we use first-principles density-functional theory (DFT) to characterize the binding of PVP repeat units to Ag(100) and Ag(111) surfaces. These studies indicate a binding preference of PVP to Ag(100) that is consistent with experimental observations. To understand the solution-phase binding of PVP to these Ag surfaces, we develop a new metal-organic many-body (MOMB) force field with high fidelity to DFT. We implement this force field in molecular-dynamics (MD) simulations to characterize the potential of mean force and the mean first-passage times for solution-phase Ag atoms to reach PVP covered Ag

facets. Using these mean first- passage times, we predict kinetic Wulff shapes of large Ag nanocrystals (around 100 nm) and show that these should be {100}-faceted cubes. We also use MD simulations to characterize the interfacial free energies of PVP-covered Ag facets in solution. The thermodynamic Wulff shapes that we predict in these calculations exhibit {111} facets. These findings are consistent with experimental observations that suffciently small Ag nanocrystals with sizes ≤ 20 nm are not {100}-faceted and larger nanocrystals become {100}-faceted in the presence of PVP.

In experimental studies, Cl⁻ is often added in the synthesis of Ag nanocubes to achieve "pointy" corners. We use *ab initio* thermodynamics to characterize the surface energies of various Cl covered surfaces as a function of the solution-phase Cl⁻ chemical potential. Our studies indicate that Cl adsorption can enhance the thermodynamic tendency for {100}-faceted Ag nanocubes, in agreement with experiment.

2:30 PM BREAK

3:30 PM BM03.07.03
Predictive Engineering of High-Density Lipoprotein-Mimetic Nanomaterials—Structural and Functional Analysis on Paraoxonase-1 Incorporation <u>Taeyoung Kim</u>, Yoshitaka J. Sei, Michael Toth, Sang Eun Jee, Seung Soon Jang and YongTae Kim; Georgia Institute of Technology, Atlanta, Georgia, United States.

Recent studies have introduced that compositional alteration of HDLs in patient with CVD or chronic kidney disease (CKD) lead to HDL functional heterogeneity. The resulting dysfunction of HDL may lead to the failure to demonstrate that raising plasma high-density lipoprotein (HDL) levels are associated with reducing cardiovascular disease (CVD). This challenge highlights the importance of better understanding of HDL functional heterogeneity. Paraoxonase-1 (PON1) is a major anti-inflammatory and anti-atherosclerotic component of HDL. However, our understanding of the mechanism with which PON1 interacts with HDL relies on the results from bare measurement of plasma HDL levels. Here, we present a new combined approach that leverages both molecular dynamics simulation and microfluidic synthesis of engineered HDL-mimetic nanoparticles (eHNPs) to predict and validate PON1 interactions with or incorporations into eHNP-A1 (apolipoprotein A1 based eHNP). We found that PON1 binds to both discoidal and spherical eHNPs, both of which have the double-belt apoA1 structure while spherical eHNPs have cholesterol in the core, but not to apoA1-free micelle structure nor to trefoil model structure for spherical eHNPs, which are composed of three apoA1's. Energy analysis of MD simulation confirmed that PON1 binds to the apoA1 helix 7 of a discoidal eHNP, while adhering to the apoA1 helix 17 and helix 18 of a spherical eHNP. More interestingly, we found that the hydrophobic N-terminal domain of PON1 (PON1-H1) serves as a binding area of PON1 to a spherical eHNP, whereas it has nothing to do with a discoidal eHNP. Furthermore, we explored possible incorporation of multiple PON1's into a single eHNPs, resulting in distinct helix interaction from the single PON1 cases. Our integrated approach will bring a new ground-breaking approach to the analysis and development of engineered nanomaterials as well as analysis of natural nanocomposites, addressing the current challenge of costly and vague experimental approaches to the measurement and quantification of complex nanomaterials.

3:45 PM BM03.07.04
Determining of the Structure of Rosette Nanotubes Using Multi-Scale Molecular Modeling—Ring Stack vs Helical Tube Arthur A. Gonzales[2, 1], Hector Grande[1], Takeshi Yamazaki[3] and <u>Hicham Fenniri</u>[1]; [1]Chemical Engineering, Northeastern University, Boston, Massachusetts, United States; [2]Chemical Engineering, University of the Philippines, Quezon City, Philippines; [3]Vancouver Prostate Centre, Vancouver, British Columbia, Canada.

Rosette Nanotubes (RNTs) are tubular soft materials self-assembled from guanine-cytosine (GΛC) hybrid molecules, which can be covalently functionalized for use in various applications. They have been shown to be effective assemblies in regenerative medicine, drug display and delivery, and catalysis.

Previous spectroscopic studies suggest they have a structure which is formed by hexameric rings, maintained by self-complementary hydrogen bonds, that are further stacked and supported by π-π interactions, which form the ring-stacked RNTs. While this mode of association maximizes the hydrogen bonding interactions and results in efficient π-π stacking, it is also possible to envision that the GΛC modules assume a helical organization defining a tubular core. We investigated this possibility by using the lysine-functionalized RNT (K1-RNT) and applying multi-scale molecular modeling methods, which include Monte-Carlo conformational search, molecular dynamics, and the statistical mechanical theory of molecular liquids, 3D-RISM theory. We considered three structures of the K1-RNT: stacked arrangement (ST), left-handed helical coil (LHT), and right-handed helical coil (RHT). Our results suggest that the formation of ST, LHT, and RHT K1-RNTs in water are favorable and are enthalpically driven. Moreover, 3D-RISM analysis suggests that the RHT conformation is more probable than the ST and LHT RNTs and this is due to a more favorable solute-solvent interaction energy. Using the 3D distribution of solvent sites around the RNTs (from 3D-RISM calculations), we were also able to determine the solvation structure and estimate the free energy of binding of each water molecule in the RNT channel. The results also corroborate the higher probability of occurring for the RHT nanotubes. Further experimental studies are underway to verify these findings.

4:00 PM BM03.07.05
Specific Adhesion and Non-Specific Adhesion of Nanoparticles Influenced by the Surface Charge of Plasma Membranes <u>Shayandev Sinha</u>, Haoyuan Jing, Harnoor S. Sachar and Siddhartha Das; University of Maryland, College Park, Maryland, United States.

Nanoparticle (NP) driven drug delivery is widely preferred for its target specificity and effectiveness. But it is a well-known problem that this technique cannot eliminate the non-specific adhesion (NSA) to healthy cell, which in turn leads to cytotoxicity. Specific adhesion can only occur when the NP can adhere to the surface of the plasma membrane through the receptor-ligand (R-L) bond formation. The surface charge of plasma membrane and the presence of the Electric Double Layer (EDL) around the cells can change this scenario in such a way that the electrostatic repulsion of the negatively charged plasma membrane and the negative charge induced on the NP might not be enough to overcome the van der Waals attraction and the thermal fluctuations. In those cases, the surface effects will play a role in engulfing the NP and cause the NSA. Here we propose an electrostatically motivated design of NPs and also propose to cover the NPs with a lipid bilayer thus making them biomimetic. We show that doing so we will have a condition where we can resist NSA and increase the chances of specific adhesion. On the other hand, a bare NP in specific cases can be of use to deliver drugs to cells that have stiffer membranes—a very common case in cholesterol rich systems. We show that tuning the ionic environment can lead to adhesion of NPs on cells with stiffer membranes. We would discuss about the membrane surface charge and salt concentration phase-space where such situations are possible.

4:15 PM BM03.07.06
Nanoparticles Organization Controls Their Potency as Universal Glues for Polymer Interfaces <u>Nicola Molinari</u>[2, 1] and Stefano Angioletti-Uberti[1, 3]; [1]Imperial College London, London, United Kingdom; [2]SEAS, Harvard University, Cambridge, Massachusetts, United States; [3]Beijing University of Chemical Technology, Beijing, China.

In recent years, nanoparticles (NP) have been shown to have the potential to answer the centuries-old question of how to mechanically strengthen an

interface between soft materials. The wide range of tunable parameters and properties make glues composed of nano-sized particles appealing to a variety of fields and applications. Despite the simplicity of the idea, the design of novel and universal adhesives based on NPs would benefit from a deeper understanding of the parameters that concur to determine the final adhesion strength.

Using a molecular-simulations-based approach we investigate the trends in, and the fundamental drivers of, the mechanical reinforcement of NP-reinforced interfaces between polymer melts. A coarse-grained model is adopted to describe both the polymer melt and the nanoparticles, and the systems are uni-axially strained and stress-strain curve constructed. We shine light on the interplay of three key properties: size of the NPs, strength of the NP-polymer interaction, and NP density. Our main result shows a non-monotonous strengthening of the mechanical response depending on the layering of the nanoparticles at the polymer interface, which we are able to identify and quantify thanks to the molecular resolution of the computer experiments. Our results confirm recent experimental speculations made to justify the existence of a maximum reinforcement at different NPs' density. Furthermore, our findings are in good qualitative agreement with a simple analytical model of the melt adhesive energy that we adapted from the literature. The results from this investigation help disentangling the contributions to the strengthening of the interface and can be used as a guide to experimental design of nanoparticles-based adhesives.

4:30 PM BM03.07.07
Tuning Self-Assembly of Oppositely Charged Nanoparticles for Controlling Bulk Heterojunction Morphology—A Multiscale Modeling Approach Soumitra Satapathi, Kulveer Singh and Prateek K Jha; Indian Institute of Technology Roorkee, Roorkee, India.

Using kinetic Monte Carlo simulations of a simple coarse-grained model, we demonstrate that the self-assembly of oppositely charged nanoparticles is a promising approach to design efficient bulk heterojunction (BHJ) solar cells. Simulations are performed starting from a random configuration of oppositely charged nanoparticles in solution for a range of concentrations. Interconnected percolated morphologies form at high nanoparticle concentrations, when the aggregate growth ceases after certain time. If only Coulombic interactions are present, the observed morphologies have very high interfacial area but too small domain size, whereas optimum values of both the interfacial area and domain size are desired for BHJ. We therefore propose and establish that an additional hydrophobic attraction between nanoparticles of same type is desired to obtain the ideal BHJ morphology. We also discuss the effects of solvent dielectric constant and the size- and charge-asymmetry of nanoparticles, which may provide additional means to control the BHJ morphology.

4:45 PM BM03.07.08
Gold Nanoparticle Translocation into Lung Surfactant—Unraveling its Mechanism at the Molecular Scale Sheikh Imamul Hossain[1], Neha S. Gandhi[3], Zak Huges[2] and Suvash C. Saha[1]; [1]School of Mechanical and Mechatronic Engineering, University of Technology Sydney, Sydney, New South Wales, Australia; [2]School of Chemistry and Biosciences, The University of Bradford, Bradford, United Kingdom; [3]School of Mathematical Sciences, Queensland University of Technology, Brisbane, Queensland, Australia.

Lung surfactant (LS), a very thin layer inside the alveolus of the lung composed of phospholipids (PL) and proteins and considered the first biological barrier of inhaled nanoparticles (NPs). LS stabilizes and protects the alveolus during its continuous compression and expansion by fine-tuning the surface tension at the air-water interface. Previous multiscale modelling studies have reported the biophysical function[1] of LS monolayer and its role, but many open questions regarding the consequences and interactions of airborne nano-sized particles with LS monolayer remain. In spite of gold nanoparticles (AuNPs) having a paramount role in biomedical applications[2], the understanding of the interactions between bare AuNPs (as pollutants) and LS monolayer components still unresolved. Continuous inhalation of NPs increases the possibility of lung ageing, reducing the normal lung functioning and promoting lung malfunction, and induce serious lung diseases such as asthma, lung cancer, acute respiratory distress syndrome, and more. Different medical studies[3] have shown that AuNPs can disrupt the routine lung functions of gold miners and promote the respiratory diseases. In this work, coarse-grained molecular dynamics simulations are performed to gain an understanding of the interactions between bare AuNPs and LS monolayer components at the nanoscale. These simulations take into account two different surface tensions at the interface to mimic biological process of breathing (inhalation and exhalation). It is found that the NPs affect the structure and packing of the lipids by disordering lipid tails and, at high concentrations, cause pores to form in the monolayer. The rupture in the LS monolayer disrupts the normal breathing process. Our results show the ability of lowering surface tension decreases with the increase of AuNPs concentration (0.01-3.6% mol, Au/lipid), in agreement with the experimental hypothesis[4]. Overall the analysed results suggest that bare AuNPs impede to lower the surface tension during compression, a finding that has beneficial consequences the potential development of various lung diseases.

References
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SESSION BM03.08: Multiscale Modeling of Soft Materials and Interfaces VII
Session Chairs: Siddhartha Das and Meenakshi Dutt
Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Back Bay B

8:15 AM BM03.08.01
The Molecular Sciences Software Institute Jessica Nash; The Molecular Sciences Software Institute, Virginia Tech, Blacksburg, Virginia, United States.

The Molecular Sciences Software Institute (MolSSI) is a nexus for research, education, and cooperation serving the worldwide community of computational molecular scientists - a broad field including of biomolecular simulation, quantum chemistry, and materials science. The Institute focuses on the software infrastructure, education, standards, and best-practices that are needed to enable the molecular science community to open new windows on the next generation of scientific Grand Challenges, ranging from the simulation of intrinsically disordered proteins associated with a range of diseases to the design of new catalysts vital to the global chemical industry and climate change. The MolSSI is working to enable the computational molecular sciences community to work together to leverage its diverse capabilities that will reduce or eliminate the gulf that currently delays by years the practical realization of theoretical innovations. Ultimately, the Institute will enable computational scientists to tackle problems that are orders of magnitude larger and more complex than those currently within our grasp. This lecture will provide an overview of the Institute's activities, goals, and vision.

8:30 AM BM03.08.02

Hybrid Simulations of Gas Permeability of Carbon Nanotube Network Materials <u>Alexey N. Volkov</u>, Omid A. Ranjbar and Md Abu Horaira Banna; University of Alabama, Tuscaloosa, Alabama, United States.

Carbon nanotube (CNT) network material, including buckypaper, films, vertically aligned arrays, and aerogels, are microporous materials that can be used for gas separation, purification, and storage. Scaffolds of CNTs can be also used as reinforcement in nanocomposite materials, fabricated by chemical vapor deposition, chemical vapor infiltration, or atomic layer deposition of inorganic materials on networks of carbon nanotubes. Utilization of the potential of CNT materials in these applications requires understanding of relationship between structural properties of random CNT networks and their gas permeability. The goal of this work is to develop a hybrid computational approach for simulations of gas flows through networks of CNTs, as well as deposition from the gas phase on CNT surface. Our computational model includes (1) a mesoscopic model of CNT materials, (2) an atomistic-mesoscopic model of molecular motion through a random network of nanotubes, and (3) a gas kinetic model of gaseous flow through CNT materials. In the mesoscopic model, every nanotube is represented by a chain of cylindrical segments. This model is used to generate samples of CNT films and aerogels with well-defined structural properties, including bundle and porous size distributions, in dynamic simulations of self-assembly of dispersed nanotubes into networks of bundles. In the atomic-mesoscopic model, gas flows through generated CNT networks are simulated using molecular dynamics-type approach based on direct solution of equations of motion of individual gas molecules. In this model, gas molecules interact with a fixed CNT network through a specially designed mesoscopic force field that accounts for the absorption of molecules at the CNT surfaces. The gas kinetic model is used to study the diffusion process at larger length scales that are not accessible in mesoscopic simulations. In this case, the material sample is modelled by a regular two- or three-dimensional arrays of straight CNT bundles with structural parameters that resemble the average structural parameters of in silico generated material samples. The gas kinetic model is implemented in the form of the Direct Simulation Monte-Carlo method, where interaction of gas molecules with CNTs is described by the model of diffuse scattering. This hybrid approach allows us to study gas permeability of CNT materials and material deposition in a broad range of length scales, from nanometers to millimeters. The simulations of gas permeability are performed in a range of pressure from 1000 Pa to 1 MPa and for density of CNT films and aerogels varying from 0.01 g/cm^3 to 0.4 g/cm^3. The simulations reveal the strong effect of porous structure and density of the CNT materials on self-diffusivity of gases, effective permeability, and homogeneity of deposition of materials inside CNT networks. This work is supported by the NSF CAREER award CMMI-1554589 and NASA Early Stage Innovations program (project NNX16AD99G).

8:45 AM BM03.08.03

Bio-Inspired Structural Coloration Obtained from Micro-Kirigami Photonic Structures—A Computational Study <u>Amina Matt</u>[1,2], Fabien Sorin[1] and Craig Carter[2]; [1]Institute of Materials, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland; [2]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural coloration is macroscopic phenomenon resulting from the interaction of light with microscopic, i.e. sub-wavelength, structure features. It is naturally observed in diverse applications, notably the vivid blue color of certain butterfly wings, due to a combination of elementary optical processes such as thin-film interference and diffraction gratings. Recently, the dynamical effects of such artificial structures under stresses and deformations have received a great deal of attention, hinting towards tunable bio-inspired materials. Simple photonic structures have succeeded in replicating bright and vivid structural colors observed in nature, while more complicated structures address the issue of angle-dependent reflectivity, achieving a stable color across wide viewing angles with the introduction of irregularity but at the cost of manufacturing complexity.
Here, we suggest and illustrate an alternative approach using micro-kirigami photonic crystals, which achieves bright and vivid colors across wide viewing angles and allows tunability of the obtained color. Micro-kirigami are three dimensional buckled structures, obtained from the deformation of two dimensional materials with patterned microscopic cuts. Recent advances in the field have extended such techniques to the obtention of mesoscale structures from micro/nanomembranes with complex shapes resulting upon buckling from the wide variety of cut patterns [1]. The demonstration of micro-kirigami structures could lead the way further in the miniaturization of such assemblies.
Numerical calculations on periodic arrays of simple polymeric ribbons with parallel cuts and more complex micro-kirigami structures, exhibit the required design objectives. The introduction of irregularity, facilitated by the notch patterning, helps stabilize the obtained color across a range of viewing angles while tunability is inherent in the buckling process. The large parameter space is efficiently optimized using a combination of Finite Element and Finite Difference Time-Domain modelling to produce various structures with bright and stable colors.
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9:00 AM BM03.08.04

Using Simulations of Rare Earth Elements in Aqueous Solution, in Organic Acid Complexes and at Interfaces to Suggest Improved Processing Routes <u>Aaron Finney</u>[1], Sebastien Lectez[2], Linghan Kong[1], Colin L. Freeman[1], Stephen Stackhouse[2] and John H. Harding[1]; [1]Materials Science and Engineering, The University of Sheffield, Sheffield, United Kingdom; [2]School of Earth and Environment, University of Leeds, Leeds, United Kingdom.

Researchers are searching for more efficient and environmentally-friendly extraction and processing methods. This is particularly true in the case of rare earth elements (REEs), the security of supply of which has been identified as 'critical'. [1] New and sustainable extraction, processing and recycling methods for REEs are urgently needed. Since REEs can be mobilised and concentrated in hydrothermal fluids [2] and from easily leachable clays [3], fractionating REEs from solution offers a cheap way to increase their yield from deposits. Biologically active molecules, such as organic acids can accumulate specific groups of REEs from solution, [4] and so understanding their action should help to design better additives for materials processing. In the present study, density functional theory and classical force field molecular dynamics have been applied to investigate Nd^{3+}, Gd^{3+} and Er^{3+} REEs in solution. The solvation structure, energetics and mobility of REEs compared well with experimental measurements. Ligand binding simulations were performed with common anions, *e.g.* chloride, and organic acids using advanced sampling methods—including Umbrella Sampling and metadynamics—and complex stability constants were calculated. Ligand exchange mechanisms and preferential organic acid binding to REEs were characterised by analysis of free energy surfaces. Our results show that ion size is crucial for the type of ligand exchange mechanism.
Simulations were performed to understand the sorption of REEs onto kaolinite clays where they are often found in nature. By studying reversible exchange reactions for REE binding at the kaolinite–solution interface we can quantify the strength of interaction and identify barriers to REE release for processing. Furthermore, the simulations, by spanning light to heavy REEs (Nd to Er), allow us to investigate why REE clay deposits are a good source for heavy REEs. Combined, these simulations at the nanoscopic level provide new information to aid in the design of REE processing methods from unconventional deposits in the search for economical, environmentally friendly ways to secure REE supply.

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9:15 AM *BM03.08.05
Active Micromechanics of Blood Clot Contraction <u>Alexander Alexeev</u>; Georgia Institute of Technology, Atlanta, Georgia, United States.

Blood clotting is the final step in hemostasis resulting in the sealing of an injured blood vessel and the bleeding arrest. Clotting is a highly complex multi-stage and multi-scale process involving platelet activation, polymerization of fibrin networks, and development of a platelet-fibrin hemostatic plug in the damaged vessel that retracts to restore normal blood flow. Blood clotting disorders may result in a variety of life threatening conditions, including excessive bleeding, stroke, and heart attack. Understanding of the physics underlying the clotting process is critical for effective treatment of these and other blood disorders. We develop an experimentally-informed mesoscale model to obtain fundamental insights into the active process of blood clot contraction. We employ the model to examine how the clot size and microstructure evolve in time due to the fibrin-platelet interactions and to explore the role of the platelet activation pattern in the clot contraction kinetics. Our results pinpoint the critical role platelet heterogeneity plays in the effective clot contraction.

9:45 AM BREAK

10:15 AM BM03.08.06
Drop on Superhydrophobic Soft Surface-Towards Designing Self-Cleaning Soft Surfaces Haoyuan Jing, Parth Rakesh Desai, Yanbin Wang, Shayandev Sinha and <u>Siddhartha Das</u>; University of Maryland, College Park, Greenbelt, Maryland, United States.

A liquid drop on a soft elastic surface equilibrates by selecting a contact angle demonstrated by Neumann's law. A hydrophobic drop itself deforms and causes a deformation in the substrate. Studying this phenomenon necessitates a combined macroscopic and microscopic description of the contact angles. We develop new scaling theory to quantify the interplay of the two effects of drop wetting, i.e. the drop compressing the polymer brush and the polymer brush repelling the drop. Our scaling theory predicts that for a case of low stiffness the polymer compression is independent of stiffness and for high stiffness there is a monotonous decrease of polymer compression due to its interaction with the droplet. To verify this scaling theory, we perform molecular dynamics simulation of a 2-D LJ droplet wetting a flat polymer brush grafted plate. We simulate a case where the polymer brush is solvophobic. We find that the drop causes a deformation in the polymer brush that agrees quantitatively with the scaling theory we develop. We also find that the stiffness of the polymer can cause and influence the motion of the drop on the surface of the polymer grafted plate. Our theory, which is verified by MD simulations, predicts that the stiffness of polymer brush will cause the transition of the equilibrium contact angle from Young's law (rigid limit) to Neumann's law (soft limit). Our scaling theory will be useful in development of self-cleaning surfaces, and in the development of new nanofluidic devices.

10:30 AM BM03.08.07
Impact Damping at Suture Interfaces <u>Nayeon Lee</u>[1], Lakiesha N. Williams[1, 2], Sungkwang Mun[1], Hongjoo Rhee[1, 3], Raj Prabhu[1, 2] and M F. Horstemeyer[1, 3]; [1]Center for Advanced Vehicular Systems, Mississippi State University, Mississippi State, Mississippi, United States; [2]Agricultural and Biological Engineering, Mississippi State University, Mississippi State, Mississippi, United States; [3]Mechanical Engineering, Mississippi State University, Mississippi State, Mississippi, United States.

The stress wave dissipation in sinusoidal patterned interfaces that were inspired by biological sutures was investigated using Finite Element (FE) analysis. Although man-made shock absorbers such as car bumpers or guardrails are designed to absorb impact energy through plastic deformation, biological materials do not use this strategy as severe plastic deformation may cause fatal damage. Biological materials use elastic and viscoelastic responses effectively to dampen impacts and absorb energy in an effort to maintain structural integrity. In nature, suture joints are found where two stiff components interlock each other and where dynamic impacts are needed to be dissipated. For example, in mammalian skulls, turtle shells, woodpecker beaks, and ammonoid shells, a wavy sinusoidal interface was observed. An idealized bar with a sutured interface (i.e., sutured bar) and an idealized bar with a flat interface (i.e., unsutured bar) were created and analyzed from two-dimensional FE analysis in Abaqus/Explicit under dynamic conditions. FE results from this study show that a sutured interface decreased the pressure 37% more than an unsutured interface did, which arose from wave scattering and energy dissipation via interaction between the viscoelastic material in the gap and sinusoidal boundaries. Wave scattering is an interaction of waves with a boundary resulting in wave reflection, transmission, or refraction. Since the compressive incidence impinged the sinusoidal interfaces, stress wave scattering resulted in converting compressive waves (S11) into flexural waves (S22) and shear waves (S12). This decreased both the peak pressure (attenuation) and wave speed (dispersion). Also, higher strain energy occurring at sutured interfaces brought energy loss within the viscoelastic gap. Several variables related to the suture interfaces for their influence on stress wave mitigation were also parameterized. The following seven parameters were examined in this study: 1. waviness of suture (ratio of suture height to suture period), 2. ratio of the suture height over the entire structure thickness, 3. gap thickness, 4. elastic modulus, 5. type of the boundary, 6. impact amplitude and 7. impact duration. The results of the parametric study revealed that wave attenuation increased by the following three factors; a higher ratio of the suture over the entire bar thickness, shorter impact duration, and a lower elastic modulus. Wave dispersion was caused by the following two factors: a higher ratio of the suture over the entire bar thickness and a lower elastic modulus. If the material properties and impact duration cannot be controlled in the engineering design of a structural component or system, then making the suture height greater becomes the only controllable design variable that matters. These findings can be applied to design structures that resist impact yet maintain structural integrity by optimizing sutures designs for impact scenarios.

10:45 AM BM03.08.08
Effect of Salt Ions on Adsorption of Anti-Agglomerants to Water-Hydrate Interface <u>Hadi Mehrabian</u>, Michael A. Bellucci and Bernhardt L. Trout; Chemical Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Anti-agglomerant (AA) molecules are chemical inhibitors that help prevent the blockage of oil and gas transmission pipelines due to the aggregation of gas hydrate crystals. However, the effectiveness of these inhibitors is reduced at high water content, which makes it critical to design molecules tailored for water-dominated environments. Furthermore, salinity has been shown to improve the performance of most industrially-deployed anti-agglomerant molecules, including simple quaternary ammonium salts. Understanding the energetics and mechanisms of AA-hydrate interactions in aqueous environments of varying salinity can help production chemists and flow assurance engineers design better AA molecules with reduced experimental trial-and-error. We used molecular dynamics simulations to examine the surface adsorption of a model anti-agglomerant (AA) molecule binding to a sII methane-propane hydrate in environments of different salinity. From our simulation data, we identified the preferred binding sites on the hydrate surface and characterized the equilibrium binding configurations. In addition, for a subset of these binding configurations, we calculated the standard binding free energy in different concentrations of brine using potential of mean force free energy calculations. We demonstrate that in higher salinity environments, the surface adsorption of the AAs is enhanced through two distinct mechanisms. First, the salt decreases the solubility of the AA in the solution, which increases the thermodynamic driving force for surface adsorption. Second, the salt ions create a negatively charged interfacial layer close to the hydrate surface that effectively solvates the cationic head of the AA molecule. Quantitatively, we found that the presence of 3.5 wt% and 10 wt% NaCl decreases the standard binding free energy of the long hydrocarbon tail binding configuration by 0.8 and 1.4 kcal/mol, decreases the standard binding free energy of the cationic head binding by 1.5 and 3.3 kcal/mol, and decreases the standard binding free energy of simultaneous head and tail binding by 1.9 and 4.3

kcal/mol, respectively.

11:00 AM *BM03.08.09
Multiscale Modeling of Interfaces—The Good, the Bad and the Ugly Annalisa Cardellini, Matteo Fasano, Matteo Alberghini, Eliodoro Chiavazzo and Pietro Asinari; Politecnico di Torino, Torino, Italy.

In this talk, a ''good'', a ''bad'' and an ''ugly'' stories will be telling around the behaviour of water at nanoscale solid-liquid interfaces. The understanding of water transport in nanoconfined configurations has revealed a prominent significance to predict the performance of biomedical phenomena and to guide the rational design of other engineering devices.

First, molecular dynamics simulations are used to compute the self-diffusion coefficient of water within nanopores, around nanoparticles, carbon nanotubes and proteins. For almost 60 different cases, the diffusion coefficient is found to scale linearly with a dimensionless parameter which represents the confinement degree of the water molecules [1]. Such relationship, coupled with the ''good'' understanding of water transport behaviour, has shown to accurately predict the response of contrast agents for magnetic resonance imaging [1]. Later on, this relationship has been experimentally and independently validated by the Oak Ridge National Laboratory, beyond biomedical applications [2].

Second, experiments and atomistic simulations are used to elucidate the non-trivial interplay between nanopore hydrophilicity and the overall water transport through zeolite crystals. A poor correspondence between the experiments and simulations has suggested the presence of a ''bad'' surface diffusion resistance at the interface between the zeolite porous matrix and water [3]. This suggests future experimental works to address these surface imperfections, as an essential prerequisite for improving water permeability of such membranes.

Finally, the complexity of water-solid interfaces will be fully revealed by "ugly'' surfactants wrapping nanoparticle (NP) in aqueous solutions. Despite the large use of nanoparticle suspensions, tuning NP interactions and identifying desired NP assembly processes, in presence of surfactants, still represent a challenge for the design of nano-suspensions. We present a multiscale model for investigating nanoscale interfacial phenomena, stability, and aggregation of nanoparticles in aqueous solutions, including the dynamics of realistic surfactants [4]. In addition, the developed multiscale model is able to predict thermal properties of NP suspensions in reasonable agreement with the relevant experimental data from the literature, overcoming limitations of traditional theories obtained by coupling the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory with the kinetic theory of aggregation. Our results will enable the formulation of design rules for engineering NP aqueous suspensions suitable for a wide range of applications.

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11:30 AM BM03.08.10
How Graphene Inclusions Increase Mechanical Toughness of Epoxy Resins Maxime Vassaux, Robert Sinclair, Robin Richardson, James Suter and Peter Coveney; University College London, London, United Kingdom.

Adding graphene to an epoxy matrix is experimentally known to improve its mechanical properties [1], most specifically enhancing toughness. The mechanisms responsible for this increase of dissipated energy at failure are far from clear [2]. By means of molecular dynamics simulations, we have explored the interactions between pure small graphene sheets (~10 Nm) and a crosslinked epoxy network, but the 2d nanoparticles do not appear to enhance the properties of the original polymer. Conversely, in the case of previously studied clay and linear polymer nanocomposites [3], the strength of the resulting nanocomposite is reduced and the interaction energy between the sheet and the network remains relatively low. The difference in behaviour is due to the high degree of crosslinking found in epoxy resins.

It appears that the benefits of adding graphene arise at larger scales, in particular at the continuum level. At the atomic scale the toughening is not observed because the single defect doesn't induce diffuse cracking but merely the fatal crack. In order to investigate mechanisms emerging in the transition from atomic to continuum descriptions, we have implemented a concurrent multiscale model based on the heterogeneous multiscale method [4]. Using this method we can in turn explore how an isotropic distribution of nanoparticles influence the fracture processes.

Furthermore, due to processing limitations, pure graphene is rarely employed in nanocomposites and is often replaced by oxidized graphene. Hence our proposed methodology is also applied to provide insights on the influences of bonded and non-bonded interactions between the polymer and the sheets on emerging mechanical properties.

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SESSION BM03.09: Multiscale Modeling of Soft Materials and Interfaces VIII
Session Chairs: Jane Lipson and Jessica Nash
Thursday Afternoon, November 29, 2018
Sheraton, 2nd Floor, Back Bay B

1:30 PM BM03.09.01
Modelling Scotch Tape Exfoliation of Graphene Robert Sinclair, James Suter and Peter Coveney; Chemistry, University College London, London, United Kingdom.

Graphene based nano-composites hold great potential as novel and practical materials. Their manufacture has been held back by difficulties in controlling the synthesis of graphene and the subsequent dispersion into a polymer matrix. Much research has been devoted to understanding these processes through

simulation. In this research, we observe for the first time the experimentally reported behaviour in simulations of the famous Scotch tape experiment, the first method devised to exfoliate graphene. Our research also enlightens us to graphene's unusual behaviour when in a superlubric state [1], which is currently impossible to observe experimentally.

These observations are possible thanks to a new force-field, GraFF, that has been developed to better describe the friction and exfoliation of graphene and graphite in simulation. We discuss the improvements GraFF offers with respect to experiment and DFT results. GraFF recreates the adsorption of graphene sheets and the superlubric behaviour observed between nanoflakes.

With our improved understanding of graphene-graphene interactions we predict that it is significantly easier to exfoliate graphene via a peeling mechanism, rather than a shearing mechanism which is commonly believed to be case. We also discuss the mechanisms which make this possible and the techniques and materials that can be used to improve the process.

A satisfactory method of processing graphene for the advanced materials industry remains elusive; to improve the situation, a good understanding of these fundamental processes is necessary. Here we provide the insights about such processes which should foster the discovery of new routes to exfoliate graphene.

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1:45 PM BM03.09.02
Two-Wavelength Wrinkling Patterns in Helicoidal Plywood Surfaces—Imprinting Energy Landscapes onto Geometric Landscapes Alejandro D. Rey; McGill University, Montreal, Quebec, Canada.

We present a model to investigate the formation of two-length scale surface patterns in biological and synthetic anisotropic soft matter materials through the high order interaction of anisotropic interfacial tension and capillarity at their free surfaces. The unique pattern-formation mechanism emerging from the presented model is based on the interaction between lower and higher order anchoring modes. Analytical and numerical solutions are used to shed light on why and how simple anisotropic anchoring generates two-lengthscale wrinkles whose amplitudes are given in terms of anchoring coefficients. The novel finding is that the surface energy landscape with its maxima and minima can be imprinted onto the surface geometric landscape. Symmetry relations and scaling laws are used to provide the explicit relations between the anchoring constants and surface profile of the two length scale wrinkles. These new findings establish a new paradigm for characterizing surface wrinkling in biological liquid crystals, and inspire the design of novel functional surface structures.

2:00 PM BM03.09.03
The Effect of Lanthanum Doping and Oxygen Vacancy on Perovskite, Pyrochlore Oxide and Lanthanide Titanates—A First Principle Study Amar Deep Pathak[1], Foram Thakkar[1], Suchismita Sanyal[1], Hans Geerlings[2] and Arian Nijmeijer[2]; [1]Shell Technology Centre Bangalore, Bangalore, India; [2]Shell Global Solutions International, Amsterdam, Netherlands.

Fuel cells have attracted enormous interest due to their high efficiency to convert chemical energy into electrical energy with very low emission. It can be used in stationary, portable, and transport power generation. It also reduces the CO_2 emission when compared with the conventional hydrocarbon fuels, therefore considered as environmentally clean energy source. Fuel cells are classified based on the electrolyte/electrode material and operating temperature range. Solid oxide electrolyte based fuel cells operate at high temperature and are the most efficient fuel cells. They can handle variety of fuels such as H_2, CO and various hydrocarbons CH_4. [1-2]

Perovskite is a family of compound having ABX_3 type crystal structure, where A and B are cations whereas X is an anion. They exhibit variety of properties due to ferroelectric, dielectric, pyroelectric, and piezoelectric behaviours. There is paramount interest to replace conventional Ni-YSZ cermet electrode with doped perovskite in solid oxide fuel cell [3]. $SrTiO_3$, a member of perovskite family, is a well-known band insulator. Doping of La significantly enhance the electronic conductivity of $SrTiO_3$ [4]. Experimentally, perovskite ($LaTiO_3$), pyrochlore oxide ($La_2Ti_2O_7$) and lanthanide (La_2TiO_5) phase can coexist at higher temperatures ($\sim$1500 °C) [5]. Thus, it is essential to investigate the effect of doping in these phases of La and Sr. To satisfy the valancy, O vacancy is created in pyrochlore oxide and lanthanide phase after Sr doping.

In the present study, we have used GGA-DFT to investigate the various La doped structures of $SrTiO_3$, Sr doped structures of $La_2Ti_2O_7$ and La_2TiO_5 and O vacancy in Sr doped structures of $La_2Ti_2O_7$ and La_2TiO_5. The concentration of dopant is varied between 0-100 % considering all possible configurational structures. We have varied the concentration of dopant to establish its dependence on electronic energy, band gap, fermi level and formation enthalpy. We have also estimated the elastic properties of these phases. We observed a band insulator to a metallic behaviour by doping La in $SrTiO_3$. It became band insulator again after 100% La replacement in $SrTiO_3$. Such behaviour is not observed in the pyrochlore oxide phase. At the end, we shall report the preferential doping among these phase in a mixture where they all can coexist.

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2:15 PM *BM03.09.04
From Quantum to Continuum—Multi-Scale Modellng of Nanocomposites Peter Coveney; University College London, London, United Kingdom.

It is widely anticipated that many future materials will be engineered at the nano-scale, be comprised of dissimilar materials, and possess multi-functional properties and behaviour. In coming decades, *in silico* prediction and testing – that is, R&D performed on a computer – will be commonplace for these materials, in both academia and industry, given the increasing capabilities and diminishing costs of high performance computing.

There is intense current interest in use of 2-dimensional (2-d) nano-materials for these applications, including graphene and clay minerals. Composites including 2-d nanoparticles, which are sheet-like with a thickness as small as a single atom, differ from conventional materials due to the exceptionally high surface area to volume ratio of the reinforcing phase and its exceptionally high aspect ratio. This presents a major challenge for simulation technology as one has to describe a vast number of atomic interactions in the vicinity of the surface of the 2-d nanoparticle, while simultaneously accounting for how these interactions affect the properties on much larger length-scales. This is the realm of multiscale simulation, where different length and time scales are

modelled by connected "single-scale simulations".

We are working towards a multiscale computing environment to seamlessly simulate the properties of functional multicomponent 2-d materials. This is designed to encompass electronic, classical and coarse-grained molecular dynamics and continuum methods with correctly designed and implemented coupling between the levels. We aim to produce high fidelity and actionable predictions, subjected to full verification, validation and uncertainty quantification. Ultimately, the aim is to construct between the key properties of 2-d and other nanocomposites that are linked to the underlying chemical building blocks. [1,2,3]

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2:45 PM BREAK

3:15 PM *BM03.09.05
Encapsulation of Proteins with Random Copolymers Trung Nguyen, Baofu Qiao and Monica Olvera de la Cruz; Northwestern University, Evanston, Illinois, United States.

Membraneless organelles are aggregates of disordered proteins that form spontaneously to promote specific cellular functions in vivo. The possibility of synthesizing membraneless organelles out of cells will therefore enable fabrication of protein-based materials with functions inherent to biological matter. Since random copolymers contain various compositions and sequences of solvophobic and solvophilic groups, they are expected to function in non-biological media similarly to a set of disordered proteins in membraneless organelles. Interestingly, the internal environment of these organelles has been noted to behave more like an organic solvent than like water. Therefore, an adsorbed layer of random copolymers that mimics the function of disordered proteins could in principle protect and enhance the proteins' enzymatic activity even in organic solvents, which are ideal when the products and/or the reactants have limited solubility in aqueous media. Here we demonstrate via multiscale simulations that random copolymers efficiently incorporate proteins into different solvents with the potential to optimize their enzymatic activity. We investigate the key factors that govern the ability of random copolymers to encapsulate proteins including the adsorption energy, copolymer average composition and solvent selectivity. The adsorbed polymer chains have remarkably similar sequences, indicating that the proteins are able to select certain sequences that best reduce their exposure to the solvent. We also find that the protein surface coverage decreases when the fluctuation in the average distance between the protein adsorption sites increases. The results herein set the stage for computational design of random copolymers for stabilizing and delivering proteins across multiple media.

3:45 PM BM03.09.06
Miscibility and Nanoparticle Diffusion in Ionic Nanocomposites Argyrios Karatrantos[2], Yao Koutsawa[2], Philippe Dubois[3], Nigel Clarke[1] and Martin Kröger[4]; [1]Physics, Univ of Sheffield, Sheffield, United Kingdom; [2]Materials, Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg; [3]University of Mons, Mons, Belgium; [4]Materials, ETH Zürich, Zürich, Switzerland.

We investigate the effect of various spherical nanoparticles on dispersion, chain dimensions and entanglements in ionic nanocomposites for dilute and high nanoparticle loading, by means of molecular dynamics simulations.
The nanoparticle dispersion can be achieved, due to the presence of ionic bonding, in oligomer matrices, in contrast to conventional nanocomposites where the electrostatic interaction is absent.
We show that the overall configuration, as characterized by the radius of gyration, of ionic oligomer chains is unperturbed by the presence of charged nanoparticles.
In addition, nanoparticle diffusion is reduced due to the electrostatic interaction and deviates from the predictions of the Stokes Einstein relation.

4:00 PM BM03.09.07
High-Speed Contact Mechanics Between Amorphous Carbon Nanoparticles Weifu Sun and Pengwan Chen; Beijing Institute of Technology, Beijing, China.

The contact mechanics plays an important role in describing behaviours of granular matter, such as packing, flow of particles. With the development of precision processing, the high-speed motions (including translation, rolling, sliding) between nanosized building blocks are often experienced in nanodevices, such as nano-electro-mechanical system (NEMS). However, the contact behaviours between amorphous nanoparticles have seldom been explored, in particular, whether the contact models still hold or not at the nanoscale remains unknown. In this work, the dynamic behaviours between amorphous carbon nanoparticles will be studied using molecular dynamics simulations during the head-on impact and the validity of conventional continuum contact models will be tested.

4:15 PM BM03.09.08
A Coarse-Grained Molecular Dynamics Model of Single-Stranded DNA-Functionalized, Shaped Nanoparticles Benjamin E. Swerdlow[1], Fang Lu[2], Matthew Spellings[3], Julia Dshemuchadse[3], Oleg Gang[2, 5, 6] and Sharon C. Glotzer[1, 3, 4]; [1]Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States; [2]Center for Functional Nanomaterials, Energy & Photon Sciences Directorate, Brookhaven National Laboratory, Upton, New York, United States; [3]Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States; [4]Biointerfaces Institute, University of Michigan, Ann Arbor, Michigan, United States; [5]Chemical Engineering, Columbia University, New York, New York, United States; [6]Applied Physics and Applied Mathematics, Columbia University, New York, New York, United States.

Typical materials science follows a top-down approach: processing conditions influence the formed structure, dictating the key material properties. Conventional processing often limits fine control over structure-property relationships. However, advances in nanotechnology, such as DNA nanoparticle (NP) functionalization, enable a bottom-up approach for materials design. By coating NP surfaces with DNA strands that terminate in unpaired bases, specifically engineered DNA sequencing can programmatically enforce NP bonding. Yet this enthalpic basis alone is insufficient to explain all aspects of

DNA NP self-assembly: entropic parameters such as particle size and shape, as well as DNA flexibility and length, all contribute to the observed equilibrium structures. Computer simulations of these systems allow us to screen candidate building blocks and probe the effects of interactions between particles more easily and efficiently *via* computational rather than experimental exploration. Previously, a coarse-grained molecular dynamics model using the Discrete Element Method implemented in HOOMD-blue was used to simulate structures assembled in one-component double-stranded DNA (dsDNA) NP systems. Here we expand this implementation to replicate experimental results for assembly of two-component flexible single-stranded DNA (ssDNA) NPs and to predict the assembly behavior of new systems of binary shapes, where we find unique phase behavior. Our experimental studies on binary mixtures of DNA coated shaped NP are in agreement with computational results. We find that core NP shape and ssDNA flexibility are critical to self-assembly in these systems.

4:30 PM BM03.09.09
Stable Frank-Kasper Phases of Self-Assembled, Soft Matter Spheres Abhiram Reddy[2], Michael Buckley[2], Akash Arora[1], Frank Bates[1], Kevin Dorfman[1] and Gregory Grason[2]; [1]University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; [2]University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Self-assembly of soft-molecules into spherical domains adopting Frank Kasper lattices have been observed in a variety of systems, including liquid-crystalline dendrimers, charged surfactants and block copolymers (BCPs). The formation of these complex phases has been previously attributed to optimal surface area and/or volume asymmetry (polydispersity or Voronoi partition of cells) leading to the question: What selects volume asymmetry in these assemblies and how does this impact surface area of the partitions? We will address these in the context of BCPs by drawing comparisons between Diblock Foam Model (DFM) that captures the Polyhedral Interface Limit (PIL) and SCFT for diblock melts. DFM describes thermodynamics of sphere phases in terms of competing geometric quantities: surface area and dimensionless stretching (or radius of gyration) of cellular volumes enclosing domains. DFM correctly predicts not only which of these lattices is favored in equilibrium (the sigma phase) but also their relative ranking in terms of entropy and enthalpy, and their equilibrium volume distribution among spheres. Comparison to SCFT results show that increasing conformational asymmetry between blocks drives a transition to radial-chain stretching and towards the PIL described by DFM calculations. We further show that the degree of polyhedral "warping" of the spherical domains is directly correlated with the dimensionless stretching-moment of distinct cells.

4:30 PM BM03.09.10
A Computational Study on Thermo-Mechanical Characterization of Carbon Nanotube Reinforced Natural Rubber Manish Dhawan and Raj Chawla; Mechanical Engineering, Lovely Professional University, Jalandhar, India.

A computational study based on molecular dynamics simulation technique has been used to predict the mechanical and thermal behavior of carbon nanotube (CNT) reinforced natural rubber (NR) composites. A single-walled 5,5 armchair type CNT has been used for this purpose. In this study, a comparison has been made between pristine and functionalized CNTs. The functionalization groups used in this study were carboxylic (COOH), ester ($COOCH_3$) and hydroxyl (OH). The studies show the improvement in elastic properties of developed composites in the presence of functionalization group. In addition, the effect of volume fraction and 1-25% addition of functionalization group has been studied. The obtained simulation results show the better load-transfer capacity in developed polymer system and improved elastic modulus. Thermal properties of developed composite systems were studied by non-equilibrium molecular dynamics method (NEMD). The addition of functionalized CNTs shows enhanced mechanical and thermal properties.