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# MOLECULAR SIMULATIONS OF COMPLEX FLUIDS AND INTERFACES



Recent Advances and Challenges

FEBRUARY 21 - 23, 2020  
IIT KANPUR



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# About



## Welcome

Welcome to the international symposium "Molecular Simulations of Complex Fluids and Interfaces", hosted at IIT Kanpur.

The behaviour of interfaces plays an important role in several industrial and natural processes. Molecular simulations can reveal microscopic insights into the structure and properties of solid-liquid interfaces. This meeting aims to provide a forum for exchanging ideas and sharing recent scientific advances from several perspectives. It is hoped that the current state of simulation methodologies will be established, paving the way for the future development of computational tools and research.

## Topics

- Molecular Simulations: New Methodologies and Applications
- Advances in Coarse-Graining and Challenges
- Soft Matter Simulations
- Confined Fluids
- Wetting and Interfacial Phenomena
- Biomolecular Simulations
- Specific Systems and Models

# Timetable

KL: Keynote Lecture, IS: Invited Speaker, ST: Sponsored Talk.

## February 21, Friday

15:00–16:00		<b>Registration</b>	
16:00–16:15		<b>Inauguration Ceremony</b>	
16:15–17:15	KL	<b>Florian Müller-Plathe</b> Technische Universität Darmstadt	Wetting, Drying, Adhesion
17:15–17:40	IS	<b>Neelanjana Sengupta</b> IISER Kolkata	Modulating Self-Assembled Amyloidogenic States via Solvent and Temperature: Insights from Computer Simulations
17:40–18:05	IS	<b>Harshwardhan Katkar</b> IIT Kanpur	Multiscale Modeling of Actin Filaments
18:05–18:30	IS	<b>Manjesh K. Singh</b> IIT Kanpur	Rheology of Nonequilibrium Polymer Melts
19:00–21:30		<b>Reception Dinner</b>	

## February 22, Saturday

9:30–10:30	KL	<b>Edward Maginn</b> University of Notre Dame	Computational Design of New Materials for Separations and Energy Storage
10:30–11:00	<b>Tea Break</b>		
11:00–11:25	IS	<b>Beena Rai</b> Tata Research Development and Design Center	Skin Lipids and their Interfaces: A Computational Approach towards Mimicking Skin Barrier Function
11:25–11:50	IS	<b>Sudip Roy</b> National Chemical Lab, India	Bridging Scales for Simulation of Lipids
11:50–12:15	IS	<b>Swati Bhattacharya</b> IIT Bombay	Molecular Dynamics Investigations of anti HIV-1 protein SAMHD1
12:15–12:40	IS	<b>R. Sankararamakrishnan</b> IIT Kanpur	TBA
12:40–14:00	<b>Lunch Break</b>		
14:00–15:00	KL	<b>Balasubramanian Sundaram</b> JNCASR	Modelling Supramolecular Polymers
15:00–15:25	IS	<b>Divya Nayar</b> IIT Kharagpur	Microscopic View of the Crowding Effects on Hydrophobic Collapse
15:25–15:50	IS	<b>Nisanth N. Nair</b> IIT Kanpur	Exploration of High Dimensional Free Energy Landscapes of Chemical Reactions
15:50–16:20	<b>Tea Break</b>		
16:20–16:45	IS	<b>Rajat Srivastava</b> Politecnico di Torino	Thermo-Physical Properties of Graphene Reinforced Thermoplastics: A Coarse-Grained Modelling Approach
16:45–17:10	IS	<b>Tamal Banerjee</b> IIT Guwahati	Reactive Force Field Simulations on the Degradation of Quinoline
17:10–17:30	ST	<b>Ashwini Kumar</b> NEC Corp.	Vector Computing- Simulation and A.I.
17:30–18:55	<b>Poster Presentation Session</b>		
18:55–19:00	<b>Announcement of Springer Best Poster Awards</b>		

## February 23, Sunday

9:30 –10:30	KL	<b>David A. Kofke</b> SUNY, Buffalo	'Mapped Averaging' Method for deriving Ensemble Averages: Application to Crystals
10:30–11:00	<b>Tea Break</b>		
11:00–11:25	IS	<b>Shantanu Maheshwari</b> Shell Technology	Nucleation and Growth of a Nanobubble on Rough Surfaces
11:25–11:50	IS	<b>Kaustubh Rane</b> IIT Gandhinagar	The Role of Solid-Liquid Interfacial Fluctuations in the Spontaneous Motion of Droplets
11:50–12:15	IS	<b>Sandip Khan</b> IIT Patna	The Wetting Behavior of Imidazolium Based Ionic Liquids using Molecular Dynamics Simulation
12:15–12:40	IS	<b>Jhumpa Adhikari</b> IIT Bombay	Phase Equilibria of Binary Mixtures of Triangle-Well Fluids : Bulk vs Confined Systems
12:40–14:00	<b>Lunch Break</b>		
14:00–14:25	IS	<b>Sudeep Punnathanam</b> IISC Bangalore	Computing Solid-Liquid Interfacial Free Energy via Thermodynamic Integration
14:25–14:50	IS	<b>Subir K. Das</b> JNCASR	Kinetics of Clustering in an Assembly of Vicsek-Like Active Particles
14:50–15:15	IS	<b>Tarak Patra</b> IIT Madras	Correlation between Glass Formation and Ion Conductivity in Polymeric Ionic Liquids
15:15–15:40	IS	<b>Prateek Kumar Jha</b> IIT Roorkee	Multiscale Modeling Approaches in Excipient Design for Oral Drug Delivery
15:40–16:10	<b>Tea Break</b>		
16:10–16:35	IS	<b>Sk. Musharaf Ali</b> BARC, Mumbai	Microscopic Assessment of Liquid-Liquid Extraction System in Bulk and at the Interface
16:35–17:00	IS	<b>Vishwanath Dalvi</b> ICT, Mumbai	Study of Water Extraction by Phosphate Ligands by Experiments and Molecular Simulations
17:00–17:25	IS	<b>Rajat Desikan</b> Invictus Oncology Pvt. Ltd.	Accurate Computational Calorimetry of Lipid Membranes by void-induced Melting
17:25–17:35	<b>Springer Poster Awardee Talk-1</b>		

17:35–17:45	<b>Springer Poster Awardee Talk-2</b>
17:45–18:00	<b>Vote of Thanks</b>
19:00–21:30	<b>Symposium Dinner</b>

# List of Abstracts – Talks

**February 21, Friday**

## **Wetting, Drying, Adhesion**

**F. Müller-Plathe**

**KL**

Theoretical Physical Chemistry, Technische Universität Darmstadt

We will review recent advances on the simulation of small-molecule fluids as well as polymers at solid interfaces. We will cover wetting of surfaces by liquids as well as the evaporation of liquid droplets from them. We will also look at the structure formation of polymers near solid surfaces and the resulting interphase properties, such as encountered in coatings and nanocomposites.

# **Modulating self-assembled amyloidogenic states via solvent and temperature: Insights from Computer Simulations**

**N. Sengupta**

IS

Department of Biological Sciences, Indian Institute of Science Education and Research  
Kolkata, India

Self-assembled amyloid conformations are more resistant to ‘denaturation’ than the folded states of globular proteins. This corresponds, in large part, to the nature of their conformational energy landscape. Folding is typically associated with a rough, yet ‘funnel-shaped’ energy landscape corresponding to an identifiable conformational minimum. In contrast, the landscape corresponding to amyloid formation features several equivalent minima separated from highly stable ‘amyloid’ conformations by large kinetic barriers. A recurring challenge in protein biophysics has been to identify perturbative ways to disrupt stable amyloids; consequences range from proteopathic amelioration to preservation of bio-specimens. Such goals, however, necessitate molecular-level details of the response of the amyloidogenic assemblies to perturbative conditions. Herein, I will highlight first our efforts toward understanding the effects of a cosolvent in interfering with early amyloid assembly. I will then discuss our recent work on thermal conditions affecting the stability of a putative pre-formed amyloid; the overall structural response is decoupled from the thermodynamic response of the hydrophobic core, contradicting the expectations of a folded state. Further work reveals that these effects are modulated by the hydration layer in proximity to the amyloid states; this layer contains important signatures of the overall structural and thermodynamic response.

# Multiscale Modeling of Actin Filaments

H. Katkar

IS

Department of Chemical Engineering, IIT Kanpur, India

Actin is an important protein in the cellular cytoskeleton, which polymerizes into polar filaments that form dynamic actin networks including filopodia, made of parallel actin filaments bundled together. Each polar filament grows at its barbed end and shrinks at its pointed end under physiological conditions. The filament also ages as the nucleotide ATP bound to an actin subunit in the filament hydrolyzes and releases inorganic phosphate, modulating its mechanical properties and binding affinity towards several important actin binding proteins. The cooperative nature of ATP hydrolysis and phosphate release has been under debate for several decades. This work demonstrates the use of a multiscale modeling framework to gain insights into the cooperative kinetics of these reactions. Implications of molecular level cooperativity on large scale evolution of actin filaments will be discussed. Further, the role of Enabled/vasodilator-stimulated phosphoprotein (Ena/VASP), an actin binding protein that assists filopodia formation by continuously associating with the growing barbed ends of predominantly short actin filaments in the bundles, will be discussed. The structure of a wild-type Ena/VASP loosely resembles a four-arm star polymer, with each arm consisting of several important domains responsible for interactions with actin. In vitro microscopy experiments of purified actin filaments with Ena/VASP mutants of varying functionalities exhibit a rich phenomenology. A model based on kinetics of individual arms of Ena/VASP is used to understand the experimentally observed binding-unbinding rates of Ena/VASP mutants on actin filaments. The modelling framework allows us to gain useful insights into dynamics of the actin network.

# Rheology of Nonequilibrium Polymer Melts

**M. K. Singh<sup>1</sup>, K. Kremer<sup>2</sup>**

IS

<sup>1</sup> Department of Mechanical Engineering, IIT Kanpur, India

<sup>2</sup> Polymer Theory, Max Planck Institute for Polymer Research, Mainz

Polymers have become very popular in everyday use because of ease in processing of polymeric materials. Polymers are processed to different complex shapes from the molten state. Polymer melts display rich viscoelastic behaviour in the typical length and time scales. The processing of polymer melts become difficult with increase in molecular weight ( $M_w$ ). The long polymer chains in a melt have to move in a specific way due to the topological constraints "entanglements" imposed by neighbouring chains. This happens because of the fact that in a polymeric systems each monomers are connected to their neighbouring monomers and can not crossover each other. Increase in number of entanglements with increase in  $M_w$  leads to increase in viscosity. We have used complementary experimental and simulation approaches to study the development of entanglements in a fully disentangled melt of collapsed polymer chains and changes in viscosity, moduli and glass-transition temperature during the process.

## February 22, Saturday

### Computational Design of New Materials for Separations and Energy Storage

E. J. Maginn

KL

Department of Chemical and Biomolecular Engineering, University of Notre Dame

Chemical separation technologies such as distillation account for tremendous amount of the world's energy consumption. As a consequence, the National Research Council has called for the development of alternatives to distillation to meet the Energy Intensity of Chemical Processing Grand Challenge. In the first part of this talk, I will focus on ionic liquid solvents designed to preferentially separate CO<sub>2</sub> from air, methane and hydrogen. Permeabilities / separation factors are computed for ionic liquids confined in membranes and in nanoporous media. The solubility of chemically reacting ionic liquids is computed directly using a combination of quantum and classical modeling approaches. A new reactive Monte Carlo (RxMC) method is described that enables the direct calculation of the reactive absorption isotherm as a function of pressure. Energy storage technologies such as rechargeable batteries are key enablers of renewable energy sources such as wind and solar. The development of "beyond lithium ion" batteries relies upon the development of new electrolytes. In the second part of the talk, I will describe our work simulating "water-in-salt" electrolytes and deep eutectic solvent electrolytes, where we compute the structure and dynamics of these systems and compare with results from experimental collaborators.

# **Skin Lipids Their Interfaces: A Computational Approach Towards Mimicking Skin Barrier Function**

**B. Rai**

IS

Tata Research Development and Design Center, India

Human skin is a vital organ acting as an interface between us and our surroundings. It is one of the largest organ of our body comprising of three layers – Epidermis, Dermis and Hypodermis. While epidermis is responsible for overall appearance and texture of skin, its outermost layer called stratum corneum (SC) controls its barrier function. Dermis, primarily made up of collagen and elastin, provides structural support and elasticity. The deepest layer – hypodermis, is composed of adipose tissues and provides the heat resistance. SC is composed of 15–20 layers of flattened cells called corneocytes (Bricks) which are embedded in a lipid matrix (Mortar) composed of ceramides, cholesterol, and fatty acids. The “bricks and mortar” structure of SC makes it selectively permeable thus to protecting underlying tissue from infection, dehydration, chemicals and mechanical stress. While corneocytes of SC remain almost impermeable, 95

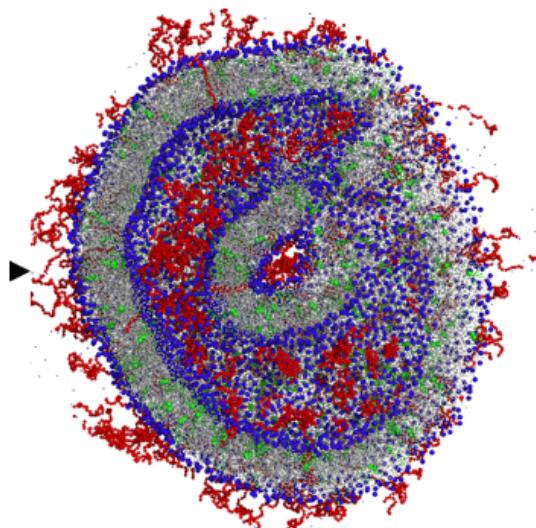
# Bridging Scales for Simulation of Lipids

S. Roy, S. Sarkar, P. R. Pandey

IS

Prescience Insilico Private Limited

The design of supramolecular nanostructures for drug delivery is hindered by a limited atomistic level understanding of interactions between building blocks. Here, we report the development of a computational algorithms integrates force-field-based models with large-scale all-atomistic explicit water molecular dynamics simulations to mesoscale simulation to design stable nanoscale lipidic supramolecular structures. In one example, we demonstrate how optimizing the ratio of excipients can help in forming stable nanoscale supramolecular assembly with different phases. In our second example we showcase the self-assembly of sophorolipids which contained hydrophilic head groups at the ends of a long hydrophobic tail. As a result of dual head groups sophorolipids can self assemble into variety of structures (morphologies) in water. Distinctions in structural arrangements of these self assembled systems along with the phase diagram as a function of concentration in water from mesoscale simulations will be presented.



Self-assembled supramolecule for drug delivery.

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## Molecular Dynamics Investigations of Anti HIV-1 Protein SAMHD1

**S. Bhattacharya**

IS

Department of Chemical Engineering, IIT Bombay, India

HIV-1 is restricted in macrophages and certain quiescent myeloid cells due to a “Scorched Earth” dNTP starvation strategy attributed to the Sterile Alpha Motif and HD domain protein – SAMHD1. Active SAMHD1 tetramers are assembled by GTP-Mg<sup>2+</sup>-dNTP cross bridges and cleave the triphosphate groups of dNTPs at a Km of 10 uM, which is consistent with dNTP concentrations in cycling cells, but far higher than the equivalent concentration in quiescent cells. HIV-2 and SIV have evolved defences against SAMHD1, underscoring its role in restriction. The regulation of SAMHD1 by phosphorylation (at T592) and Glutathione driven redox reactions has been experimentally studied and yet not properly understood. We have used correlation network analysis along with molecular dynamics techniques to study the flow of allosteric information across the active complex. I will discuss how our MD analysis has yielded insights that complement and expand X-Ray and biochemistry based models of SAMHD1 activity.

# **Role of Residues at the Membrane-Water Interface in the Selectivity of Solute Transport: Computational Studies of Formate/Nitrite Transporters**

**R. Sankararamakrishnan**

IS

Department of Biological Sciences and Bioengineering, IIT Kanpur, India

Channels and transporters are integral membrane proteins that transport solutes across the cell membranes. Many of them are selective for specific solutes. The family of Formate/Nitrite transporters (FNTs) is selective for monovalent anions [1]. The main metabolites of bacterial respiration during anaerobic mixed-acid fermentation are formate, nitrite and hydrogen sulphide. These anions become cytotoxic when accumulated in cytoplasm. Individual FNT members are involved in selectively transporting these anions. Three-dimensional structures of different FNT members indicate that they share an aquaporin-like hour-glass helical fold. Since FNTs are found only in bacteria, archaea, fungi and protists and not in mammals, they are considered as potential drug targets for many diseases caused by bacteria and fungi. Using phylogenetic analysis, we have identified eight different subgroups that include two formate, three nitrite and one hydrosulphide transporters [2]. Two subgroups, designated as YfdC- and YfdC-, are also recognized with unassigned function. We performed equilibrium molecular dynamics simulations and umbrella sampling on FNT members belonging to three representative FNT subfamilies. We evaluated potential of mean force (PMF) profiles of different solutes using umbrella sampling approach. Our simulation studies strongly suggest that the uncharacterized EcYfdC- is not likely to transport monovalent anions [3]. Its physiological function is perhaps to transport neutral solutes or even cations.

## **References**

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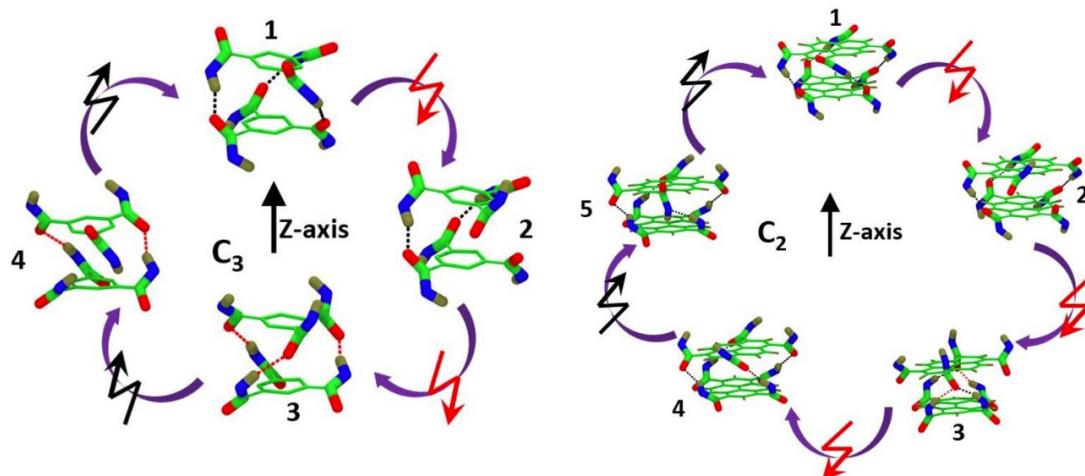
# Modelling Supramolecular Polymers

B. Sundaram

KL

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bengaluru

Unlike conventional polymers, supramolecular polymers are formed out of non-covalent interactions between monomers in solution. The relatively weaker interaction strengths makes the association between the monomers to be reversible. Molecular simulations are apt to study this self-assembly process as they possess the right tools to take into account finite temperature and bulk solvent conditions explicitly. The talk will review the vast experimental literature on this topic and will introduce the computational techniques. The application of such methods have led to the following new findings: ground state dipole configuration in the classic BTA system, dipole driven cooperative mechanism of polymerisation, reversal of chiral handedness concomitant with polarization reversal in ferroelectric thin films of supramolecular polymers, and the demonstration of isodesmicity in self-assembly, using free energy methods.



# Microscopic View of the Crowding Effects on Hydrophobic Collapse

D. Nayar

IS

Centre for Computational and Data Sciences, IIT Kharagpur, India

A living cell is a crowded milieu comprising of large-sized macromolecules, small co-solutes and ions with less free water [1,2]. Crucial biological processes involving hydrophobic collapse such as protein folding and other self-assemblies occur in this environment. However, a molecular-level understanding of these effects remains elusive. It has been widely accepted that these effects are induced due to size (steric) effects of crowders and the solvent excluded volume effects that are entirely entropic in nature [1]. This excludes the role of any direct solute-crowder or crowder-crowder attractive interactions, which however has been shown to play a crucial role recently [3]. Therefore, molecular mechanisms associated with these effects need to be further explored. We investigate the crowding effects of small (tri)peptides on collapse equilibria of a generic hydrophobic polymer. Advanced molecular dynamics simulations and statistical mechanics solvation theories are used to examine solvation thermodynamics of polymer collapse. The unresolved role of crowder intermolecular interactions is examined. Our results show that weak polymer-crowder attractions lead to strong polymer collapse only at high crowder volume fractions, involving entropic depletion of crowders from polymer surface, in accordance with the widely known depletion mechanism. Interestingly, on making the polymer-crowder attractions stronger, polymer collapses at low volume fractions and that too via preferential adsorption of the crowders on the polymer surface. Strongly interacting crowders weaken the polymer collapse at high crowder volume fractions. A transition from enthalpy-dominated to entropy-dominated polymer collapse is observed with increasing crowder concentrations. Our results provide new insights into the existing theories of crowding effects on macromolecular collapse and the talk will discuss its implications on macromolecular collapse/aggregation processes.

## References

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# **Exploring High Dimensional Free Energy Landscapes of Chemical Reactions: New Approaches and Applications**

**N. Nair**

IS

Department of Chemistry, IIT Kanpur, India

Molecular dynamics (MD) methods are widely used to study molecular level mechanism and free energetics of chemical reactions and structural transformations in soft matter systems. Biased MD simulations are employed to accelerate transitions between two metastable states on a high dimensional free energy landscape. However, the computational efficiency of biased sampling methods decreases with increasing dimensionality, which in turn severely limits the predictive power of enhanced sampling approaches. Moreover, it is preferred that the biasing energy is not leaked out to irrelevant modes. Here we propose a new method called the “Temperature Accelerated Sliced Sampling”(TASS) to overcome these limitations. This approach allows us to perform controlled exploration of a complex free energy landscape even when it is broad and unbound, like in the case of A+B type reactions, drug binding etc. TASS enables us to choose large number of orthogonal collective coordinates for enhanced-sampling. Most importantly, we can change the dimensionality and description of orthogonal coordinates for different umbrella windows. After demonstrating the accuracy of our method, I will discuss various applications including modelling enzymatic reactions.

# **Thermo-physical Properties of Graphene Reinforced Thermoplastics: A Coarse- Grained Modelling Approach**

**R. Srivastava<sup>1,3</sup>, A. Muhammad<sup>1,3</sup>, M. Fasano<sup>1</sup>, P. Pappas<sup>2</sup>, P. Asinari<sup>1</sup>**

IS

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<sup>3</sup> Equal contributing authors

Graphene, being one of the most promising material, has gained attention in scientific and industrial fields. With its superior properties, if introduced in the polymeric matrix can potentially improve material characteristics (such as thermal, elastic, electrical properties, etc). Thus, in this study coarse-grained molecular dynamic (CG MD) simulations were performed to investigate thermo-physical properties such as density, glass transition temperature, coefficient of thermal expansion, Young modulus, Poisson's ratio and thermal conductivity of graphene reinforced thermoplastics (Polypropylene/graphene (PP/Gr) and Polylactic acid/graphene (PLA/Gr) composites). Initially, we analyzed the thermo-physical properties of neat polymers (PP, PLA) and filler (Gr) using the MARTINI force field [1-2] and compared the results with experiments. Further, CG MD simulations were performed to determine the effect of graphene reinforcement on mechanical as well as thermal properties of PP/Gr and PLA/Gr composites. CG MD simulations show that Young modulus increases with increasing graphene concentration in the PP matrix, and in good agreement with experiments. Graphene reinforcement with wt. = 2% increases the elastic modulus by 35% compared to neat PP. Similarly, enhancement of 12% in elastic modulus has been observed for PLA/Gr composite with similar reinforcements. We also performed the Non-Equilibrium Molecular Dynamic (NEMD) simulation to quantify the effect of graphene inclusion on the thermal properties of the composite using the Müller-Plathe algorithm [3]. In the case of the PP/Gr composite, effect of graphene concentration on thermal conductivity is negligible; whereas, a slight increase in thermal conductivity was observed in the case of PLA/Gr composite. The thermal behavior of composite is in agreement with literature values, which also show that the graphene concentration less than 5% wt. has negligible effects on the thermal properties of the composite [4].



**Figure 1(a)** Young's modulus (E) of PP/Gr composite as function of Gr wt%. **(b)** Young's modulus (E) of PLA/Gr composite as function of Gr wt%.

## References

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## Reactive Force Field Simulations on the Degradation of Quinoline

T. Banerjee



Department of Chemical Engineering, IIT Guwahati, India

In the current study, quinoline is considered as a model Poly Aromatic Hydrocarbon where Reactive Force Field (ReaxFF) simulations are adopted to study its degradation and pyrolytic behaviour. To confirm the intermediate and final products, a range of ReaxFF MD simulations at different temperatures with NVT ensembles for a total duration of 700 ps were implemented. Five different temperatures ranging from 2500 K–4500 K are chosen so as to allow the chemical reactions to be observed at a computationally affordable time scale. We observed a qualitative experimental agreement with respect to initiation step of the quinoline hydrogenation and formation of major intermediate products such as Tetrahydroquinoline (THQ), Propylaniline (PA) and decahydroquinoline (DHQ). Most of the intermediate reactions are found to be intramolecular while intermolecular reactions dominate at higher temperatures. The main products include ammonia, ethylene, methane, ethane and acetylene. Finally, a kinetic analysis was made to obtain the rate constants and activation energies for quinoline hydrogenation.

## **Vector Computing: Simulation and A.I**

**A. Kumar**

**ST**

NEC Technologies India Private Limited

NEC has developed a Vector Engine (VE) for accelerated computing using vectorization, with the concept that the full application runs on the high performance Vector Engine and the operating system tasks are taken care of by the Vector Host (VH), which is a standard x86 server. This is the first time that a Vector Processor is integrated seamlessly into the Linux software environment. This allows the Vector Engine to concentrate on providing the best simulation AI application performance. The application runs on the Vector Engine while tasks like I/O and similar OS functions get performed by the x86 CPU, taking advantage of the integration the Linux kernel. With NEC's SX-Aurora TSUBASA VE application developer can concentrate on getting the most out of the Vector Engine and its large high speed memory engine and additionally a single core is so powerful that weak scaling applications also benefits from vectorization show better performance on the NEC SX-Aurora TSUBASA platform than other platforms (X86 or GPU) platform.

## February 23, Sunday

### Mapped Averaging Method for Deriving Alternative Ensemble Averages

D. A. Kofke

KL

Department of Chemical and Biological Engineering, University at Buffalo, SUNY

Mapped averaging is a recently published framework that provides alternative, rigorous expressions for the ensemble averages that underlie molecular simulation. [1-3] The approach introduces knowledge from approximate theories while relying on the molecular simulation to measure the deviation from the theory. The scheme also exploits the knowledge of the forces and the Hessian of the potential. In this manner, calculation of the mapped averages by molecular simulation can proceed without contamination by noise produced by behavior that has already been captured exactly by the theory, thereby yielding results of unprecedented precision with minimal computational effort. The approach can be applied in principle to any property that can be expressed as a derivative of the free energy. It does not affect sampling, so it can be used for many properties in the same simulation. We describe our recent advances in formulating and applying these methods, focusing in particular on two broad cases: (1) the free energy, which can be obtained with great efficiency via thermodynamic integration of first-derivative properties; and (2) second-derivative properties such as the dielectric constant, which are of great practical interest, but which suffer particularly from stochastic uncertainty because their evaluation is based on averaging ensemble fluctuations when performed using conventional methods. Emphasis is placed on applications to crystalline systems, where the harmonic character of the atomic motion provides an effective baseline for the mapped average. Apart from their use in the context of molecular simulation, mapped averages may also provide a new basis for developing theoretical approaches to statistical mechanical systems.

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## Nucleation and Growth of a Nanobubble on Rough Surfaces

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We study the nucleation and growth of a nanobubble on rough surfaces by using molecular dynamics simulations. A nanobubble nucleates and grows by the virtue of a heterogenous surface reaction which results in the production of gas molecules near the surface. We study the role of surface roughness in the nucleation and growth behaviour of a nanobubble. We perform simulations at various reaction rates and surface morphology and quantified the growth dynamics of a nanobubble. Our simulations show that after the onset of nucleation, nanobubble grows rapidly with radius following  $t^{1/3}$  behaviour followed by a diffusive growth regime which is marked by  $t^{1/2}$  growth behaviour. This growth behaviour remains independent of surface roughness and reaction rates over the range considered in this study. We also quantified the oversaturation of gas required for the nucleation of a nanobubble and demonstrated its dependence on the surface morphology.

# The Role of Solid-Liquid Interfacial Fluctuations in the Spontaneous Motion of Droplets

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The density fluctuations at the solid-liquid interfaces have received great attention in recent decades in the context of protein folding. In this presentation, I will discuss them in the context of droplet motion on heterogeneous surfaces. I will first discuss our efforts to understand how the above fluctuations affect the variation of solid-liquid interfacial free energy with the nature of crystalline surface. We used the grand canonical Monte Carlo (GCMC) simulations and the cumulant expansions of the interfacial free energy to relate the above fluctuations to the interfacial entropy [1]. We observed that interfacial entropy is important for the motion of droplets when the temperature varies spatially, or temporally. I will also discuss a model system where the fluctuations are expected to strongly affect the motion of droplet [2]. Here, we used the molecular dynamics simulations to study the motion of droplet, and GCMC simulations to compute the interfacial free energies. I will end the talk by discussing our efforts to rationally design the solid surfaces having the desired solid-liquid interfacial fluctuations by using the principle of Maximum Entropy.

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# The Wetting Behavior of Imidazolium Based Ionic Liquids using Molecular Dynamics Simulation

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Ionic liquids (ILs) are of particular interest due to their tunability of physical and chemical properties and a deeper understanding of their structure-property relationship is desired. Molecular dynamics (MD) simulations are performed to understand the effect of the length of the alkyl chain attached with the cation, nature of the anions and the addition of water as aqueous medium or as impurity on the wetting behavior of imidazolium-based ILs on graphite surface. The wetting behaviors of pure or aqueous IL droplets are characterized using a density profile and orientation order parameter profile, hydrogen bond profile along the axis normal to the surface as well as through interfacial tensions. Simulation of pure IL droplet on the surface at molecular level is very challenging compared to that of aqueous IL due to their inherent characteristics, including slow dynamics, strong coulombic interactions between cations and anions, bulky nature, and heterogeneity in structure and thus results in improper sampling, non-spherical droplet on the surface etc. Therefore, efficient methods are required to understand the wetting behavior of pure ILs properly. The wetting behavior of aqueous IL droplet depends on the distribution of IL molecules across the droplet. As there are many interfaces involved in case of a droplet on surface including liquid-vapor, solid-liquid, solid-vapor and three phase contact line, it is very important to understand the preferential adsorption of IL molecules in these interfaces.

# Phase Equilibria of Binary Mixtures of Triangle-Well Fluids : Bulk vs Confined Systems

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Confined fluids occur abundantly in nature (for example, in fault gouge particles and between micron-sized particles in colloidal suspensions [1]) and also, have numerous technological and industrial applications (such as adhesion, chromatography, membranes, microfluidic devices, lubricating fluid layers, gas adsorption, catalysis and enhanced oil recovery [2,3]). The properties of a fluid under confinement may be different from that of the bulk due to the geometric constraints imposed by the presence of solid walls as well as the additional wall-fluid interactions. Fluid phase diagrams of binary mixtures exhibit rich phase behavior including vapor-liquid equilibria (VLE) with or without azeotropes, vapor-liquid-liquid equilibria (VLLE) with heteroazeotropes and liquid-liquid equilibrium (LLE) under different conditions of temperature and pressure. In this study, [4] grand canonical transition matrix Monte Carlo simulations [5] are used to determine the fluid phase diagrams, at two different temperatures, in bulk and under confinement of weakly attractive slit pores, for four different types of binary mixtures: mixture 1 is symmetric, with a weakened interaction between the unlike species (unlike the other three mixtures), mixture 2 with asymmetry in size of the molecules, mixture 3 with asymmetry in the depth of the potential well and, finally, mixture 4 where both the size and well-depth are different. The triangle-well (TW) potential [6] is employed to model the fluid-fluid and wall-fluid interactions as this potential provides simple, qualitatively accurate and practical representation of the interactions present in real systems. The simple nature of the TW models enables us to obtain a qualitative understanding of the effects of the fluid-fluid potential parameters and the effect of confinement on the vapor-liquid coexistence behavior of the four different types of TW fluid mixtures described above. One motivation for the use of this simple potential model is that the effect of individual factors like molecular size and interaction strength can be studied in isolation, unlike experiments which provide the cumulative effect of all the parameters. Significant differences in the vapor-liquid coexistence behavior of the confined fluid from the bulk phase behavior are observed. Comparison of the bulk and confined systems indicate that the intersection of the liquid-liquid phase envelope with the vapor-liquid equilibrium (VLE) curve observed in the bulk phase of mixture 1 does not occur under confinement with the heteroazeotrope being replaced by VLE showing an azeotrope at lower pressures and liquid-liquid coexistence at higher pressure. A significant decrease in the area of the vapor + liquid coexistence region is noted for mixture 2. The supercritical behavior of component 2 is noted for the confined systems in mixtures 3 and 4 at both temperatures, however, the pressure-composition diagram in the bulk system shows supercritical behavior only at the higher temperature. Canonical Monte Carlo simulations were subsequently

performed on the confined systems to obtain the energy values and the density profiles along the pore width at the equilibrium points. The latter data have been utilized to explain the phase diagrams of the confined mixtures and correlate the differences in the phase diagrams to the variation in the potential parameters.

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## Computing solid-liquid interfacial free-energy via thermodynamic integration

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In this talk, we present a method to compute solid-solvent interfacial free-energies for sparingly soluble solutes via thermodynamic integration. The proposed method combines the phantom-wall method of Leroy and Muller-Plathe [1] and the Frenkel-Ladd method [2] for solid-state free energy calculation. Our proposed method included the contribution of entropy of both solid and liquid phases in the computation of the interfacial tension. We apply this method to predict the influence of solvent on polymorph selectivity during crystal nucleation of molecular solids and vapor-liquid contact angles on a solid substrate. The proposed method for computing interfacial tension can be easily implemented using the open-source molecular dynamics package LAMMPS. This can facilitate widespread adoption of this method by a large number of research groups.

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## **Kinetics of Clustering in an Assembly of Vicsek-Like Active Particles**

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In connection with phase transitions in passive matter systems, scaling properties associated with various structural and dynamical quantities have received much attention over several decades. Analogous studies are recently being carried out in active matter systems that contain self-propelling particles and are inherently out-of-equilibrium. In this talk I will discuss kinetics of vapor-liquid phase separation in one such system that has Vicsek-like alignment activity. Results from our molecular dynamics simulations show that the growth of the average cluster size and the decay of the order-parameter autocorrelation function, a probe for quantifying ageing dynamics in out-of-equilibrium systems, in this model follow power-law scaling. Furthermore, via structural analysis we show that the ageing exponent obey a bound. These results are qualitatively similar to those for passive matter systems and extend the domain of validity of scaling concepts of nonequilibrium statistical mechanics.

## **Correlation Between Glass Formation and Ion Conductivity in Polymeric Ionic Liquids**

**T. Patra**

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Polymeric ionic liquids (PILs) are promising materials to enable more environmentally stable high density energy storage devices. Realization of PILs combining high environmental and mechanical stability with maximal ion conductivity would be accelerated by an improved molecular level understanding of these materials' structure and dynamics. It is widely recognized that both mechanical properties and ion conductivity in anhydrous PILs are intimately related to the PIL's glass formation behavior. This represents a major challenge to the rational design of these materials, given that the basic nature of glass formation and its connection to molecular properties remains a substantial open question in polymer and condensed matter physics. Here we describe coarse-grained and atomistic molecular dynamics simulations probing the relationship between PIL architecture and interactions, glass formation behavior, and ion transport characteristics. Moreover, we identify strategies for improving ion conductivity by maximizing both PIL segmental relaxation rates and the extent of ion transport decoupling from chain dynamics. This study provides guidance towards the design of PILs with improved stability and ion conductivity for future energy applications.

# Multiscale Modeling Approaches In Excipient Design For Oral Drug Delivery

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Polymeric excipients are used in controlled/modified release formulations to enhance the bioavailability of poorly soluble APIs (active pharmaceutical ingredients). The actual design of such excipients is a complicated affair, since the conventional in vitro/in vivo experiments and mechanistic models do not include the effect of excipient-API complexation and how it varies with the conditions in the gastrointestinal (GI) tract. Atomistic molecular dynamics (MD) simulations that capture the detailed excipient/API chemistry are an alluring route to develop molecular design rules of such excipients, but there is always a huge disparity between the simulated and physiological time and length scales. This talk will begin with a discussion of how we can still gain some useful insights from atomistic MD simulations of such systems. This will be followed by a discussion of systematic and generic coarse-grained approaches that can take us even further.

# **Microscopic Assessment of Liquid-Liquid Extraction System in Bulk and at the Interface**

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The recent trend toward renewal of interest in nuclear power as a futuristic energy alternative demands a close cycle spent fuel reprocessing methods with a long term vision for safe management of spent fuel. Nuclear fuel cycle is important not only to reduce the high-active solid waste but also to produce the fresh fuel for 2nd generation nuclear reactor. The extent of reprocessing depends on the efficiency of the liquid-liquid extraction processes in which the radionuclides are separated from acidic aqueous solution. The most extensively used solvent in spent fuel reprocessing is tri-n-butyl phosphate (TBP) with n-dodecane as the diluent in the PUREX process. In spite of great success, there is a demand and continuing search for an alternative of TBP, specifically for spent fuels from fast breeder reactor. Among many, tri-isoamyl phosphate (TIAP) has been considered as competitor which has similar chemical and radiological stability like TBP in presence of nitric acid. In this context, thermo-physical and dynamical properties of ligand-solvent systems are required to predict the extraction efficiency for a representative system which can be obtained either by performing experiments or by molecular dynamics (MD) simulations. In that perspective, MD simulations assist to arrive at a reasonable conclusion in minimum no of trials of experiments and thus reduce the cost as well as time. Furthermore, there is a continuing endeavour at the molecular level understanding of liquid-liquid bi-phasic extraction of metal ions due to its wide level of application from pharmaceuticals to nuclear industry. Microscopic understanding of the interface between two immiscible or partially miscible liquids of any biphasic system not only has a great interest in view of mass transfer processes but also has considerable technological values in the field of chemistry, physics and biology. Due to inherent difficulty, the understanding of molecular details at liquid-liquid interface using only experimental technique is inadequate to establish the interfacial behaviour. This is mostly due to the fluidity of the interface and its concealed environment, which restricts the experimental facts. The contribution of intrinsic thickness and broadening induced by capillary waves are responsible for total thickness but the determination of these two values are perhaps not encountered for three component system. MD simulations provide a microscopic analysis of the interfacial properties of water-organic interface. The present talk will focus on evaluation of structural, thermo-physical and dynamical properties of the liquid-liquid extraction system in bulk and at the interface using molecular dynamics simulations.

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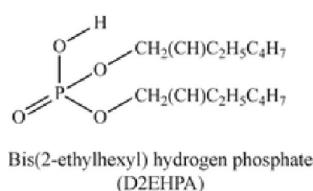
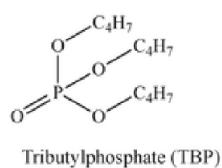
# Study of Water Extraction by Phosphate Ligands by Experiments and Molecular Simulations

D. U. Bapat, V. H. Dalvi

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Molecular level insights into structure-property relationships are essential in order to design high performance materials and chemicals. Although the first and preferred line of attack for such problems is direct experimental measurements, often puzzling aspects of macroscopic behavior of systems are hard, if not impossible, to probe experimentally at current technological levels. In such cases, molecular simulations play an invaluable role in providing microscopic insights into molecular level interactions and can thus guide experiments towards discovery or development of new materials. This talk will illustrate this point using the example of the partitioning of water into an organic phase containing phosphate ligands. Such systems are backbone of processes for reprocessing spent nuclear fuels since ligands are available that can selectively extract certain actinides from the aqueous to the organic phase. The conventional model for such partitioning is a reverse micelle of water solvated by the phosphate ligands[1]. The experimental behavior of water partitioning into a dodecane phase containing a mixture of tri-n-butylphosphate (TBP) and di-2-ethylhexylphosphoric acid (D2EHPA) ligands is counterintuitive according to this model since the D2EHPA ligand system containing both hydrogen bond donor and acceptor groups is a weaker extractant of water than a system with TBP ligands which only possess an h-bond acceptor group. Molecular simulations showed that, instead of being present in the core of a reverse micelle, water actually acts as a bridge between phosphate ligand molecules thus forming a range of supramolecular clusters: with as much as 80% of water's hydrogen bonds being formed with the extractant molecules rather than other water molecules[2].



**Figure 1:** Chemical Structure of the Phosphate Ligands



**Figure 2:** Representative figures of clusters formed are shown in parts a and b.

Extractants are depicted as VDW spheres. Water, D2EHPA, and TBP molecules are colored in red, blue, and green, respectively. In structure c, the cluster depicted in part b is shown without alkyl chain carbons and hydrogens. The cluster is rotated favorably to show the hydrogen bonding centers in the cluster. Red spheres represent the oxygens on the extractants, dark green sphere represents the phosphorus atom, and white spheres represent the hydroxyl hydrogens. Pink spheres represent water molecule oxygen (virtual site and oxygen atom).

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## **Accurate Computational Calorimetry of Lipid Membranes by Void-Induced Melting**

**R. Desikan**

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Lamellar lipid membranes exhibit a first-order gel to liquid crystalline (fluid) phase transition which is of great relevance to biological processes and industrial applications. While molecular simulations are routinely used to accurately determine such phase transitions for simple isotropic crystalline systems, no current method accurately and quickly estimates the true transition temperature of heterogeneous two-component self-assembled interfacial systems such as lipid bilayers. Here, we present a novel computational method based on void-induced kinetic melting, and employ it to accurately estimate the gel-to-fluid phase transition temperature for a 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) bilayer from extensive fully-atomistic molecular dynamics simulations, totalling  $\approx 32 \mu\text{s}$ . The method yields a unambiguous transition temperature estimate of  $T_m = 319.6 \pm 2.3 \text{ K}$  for DPPC bilayers, within a few Kelvin of the experimentally observed  $T_m = 314.5 \text{ K}$ , while the previous best estimate of  $T_m$  via conventional simulated melting with the same force-field is  $\approx 334 \text{ K}$ . Our method can be employed to assess and improve the ability of existing lipid force-fields to reproduce the gel-to-fluid phase transition, and can potentially be extended for estimating thermotropic phase transitions of multi-component lipid membranes.

# List of Posters

## Atomistic Modeling of Binary Ionic Liquid Mixtures

**N. V. S. Avula, S. Balasubramanian**

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Ionic liquids are complex fluids which show great promise in a variety of applications, from being used as electrolytes to biomass dissolution. Atomistic modeling of ionic liquids is challenging due to an interplay of different kinds of intermolecular interactions among the ions - Coulomb, dispersion and hydrogen bonding etc. Many attempts have been made to capture the essential static and dynamical properties of these liquids using empirical force field based molecular dynamics [1-3]. It is now accepted that the net charge of the ions has to be scaled down in order to reproduce experimental dynamical quantities [4]. This scaling down of charges is rationalized as a mean-field representation of polarization and charge transfer effects in the framework of non-polarizable force fields.

Generally, given a cation, the amount of charge transfer would depend on the basicity of the anion. Mondal et al. have devised a methodology to estimate the condensed phase ion charges and incorporated them into a force field framework [3]. In our recent work, we have extended this method to a mixture of ionic liquids with a common cation and two different anions [5]. We have observed that the cation charge varies linearly with composition, whereas the anion charges remain constant. This result agrees well with the X-ray photoelectron spectroscopic (XPS) studies on ionic liquid mixtures [6]. In this work, we use this linear mixing rule (of cation charge) to analyze static and dynamical properties of binary ionic liquid mixtures and compare them with experiments wherever possible. We also compare our linear mixing charge model with a popular uniform charge scaling model [1].

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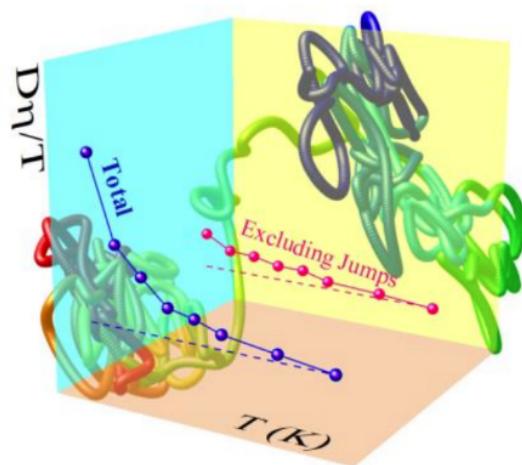
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# **Role of Translational Jump-diffusion in the Breakdown of the Stokes-Einstein Relation in Supercooled Water and its Binary Mixture with Glycerol**

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Several experiments have witnessed increasing violation of the Stokes-Einstein (SE) relation, connecting the translational self-diffusion and viscosity, in supercooled water and its mixture with different cosolvents, like glycerol, as the temperature decreases. Earlier studies explained the breakdown of the SE relation in terms of the location of the Widom line, emanating from the liquid-liquid critical point (LLCP). Although these studies made a significant contribution to understand the above phenomena, a detailed molecular picture is still lacking. Recently our group has been able to explain the SE breakdown from jump-diffusion approach [1-3]. The jump-diffusion coefficient — emanating from jump translation of water molecules — is calculated quantitatively for different temperature and pressure conditions. It is observed that the jump-diffusion is the key factor for the SE breakdown in supercooled water. The same method is adopted in the present work to explain the similar behavior in water/glycerol binary mixture at different temperatures.



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## New Age Antimicrobial Peptides: Revealing Mode of Actions of Multi Functional AMPs using Molecular Dynamics Study

**N. Desai<sup>1</sup>, S. Fox<sup>2</sup>, C. Verma<sup>2</sup>**

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Currently, antimicrobial resistance developed by many infectious pathogens is a severe emerging problem. Antimicrobial peptides can be used as potential alternatives to conventional antibiotics because of their multi functionality and non-specificity in targeting pathogens. To understand different mechanisms of killing via bacterial membrane by AMPs in detail and to see differences in the mode of action of two peptides, Magainin2 and Pleurocidin with different modes of action we performed Molecular Dynamics simulations. Experimentally, Magainin2 is known to form toroidal pores in the membrane whereas Pleurocidin is known to interact with the intracellular targets. Molecular dynamic simulations were run for both peptides and for each orientation for 100-1000 ns using Gromacs and the charmm36m force field. Modeling a bacterial membrane (POPE:POPG in 3:1) solvated in the TIP3P water model and 0.15M NaCl ions.

Magainin2 was found to significantly disrupt the membrane by forming toroidal pores, however Pleurocidin also seemed to be form pores when forced in the membrane.

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# **Tuning the Adsorption Behavior of the Material at the Molecular Scale to get the Desired Macroscopic Behavior by Using Statistical Mechanics and Molecular Simulations**

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Tuning the adsorption behavior of material to adsorb molecules or ions in the presence of some chemical species can be very useful in many applications. We need to alter the chemical nature of the material at the molecular level to get the desired macroscopic behavior. Hence it is a multiscale problem. In this poster, we describe our efforts to rationally designing the material by connecting the processes that take place at multiple scales. At the molecular scale, the knowledge of spatial distributions of different chemical species is valuable, whereas, at the macroscale, the desired behavior is expressed in terms of the quantity of adsorbate to adsorb in the presence of certain species in bulk. Our strategy is to extract the desired free-energy of adsorption from the quantities at the macroscale and then use statistical mechanics to predict the desired spatial-distributions of the chemical species at the molecular scale. We can then perform molecular simulations to compare the spatial distribution of the existing and model adsorbents with the desired values. The thermodynamic model helps us to link the desired behavior of adsorbent at the macroscopic scale with the desired spatial distribution obtained from molecular simulations.

We show the application of the strategy to design an adsorbent to selectively adsorb and desorb calcium ions in the presence and absence of a surfactant, respectively. Hence, we are rationally designing a “smart” adsorbent, a novel alternative to water-softening agents. It should facilitate adsorption and desorption (for regeneration) by using the free-energy of the system. We have performed molecular simulations on well known and commonly used adsorbents, i.e., three different types of zeolite and model adsorbent with different sigma and densities. From the molecular-scale analysis, we can get the spatial distributions of calcium ions and surfactants and no. of calcium ions adsorbed. The results from molecular simulations for natural zeolite showed an opposite trend to the desired behavior, whereas for modeled adsorbent, it showed the desired trend, but the number of calcium ions adsorbed was less than the desired amount.

# Molecular Dynamics Simulations on Interfacial Structure in Presence of Third Component

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Microscopic understanding of the interface between two immiscible or partially miscible liquids for a biphasic system not only has an immense interest in view of mass transfer processes but also has significant technological importance in the field of science and engineering. Due to its inherent difficulty, the understanding of molecular details at liquid–liquid interface using only experimental technique is not enough to ascertain the interfacial behaviour mostly due to the fluidity of the interface and buried surroundings. The contribution of intrinsic thickness and broadening induced by capillary waves ( $w_c$ ) are responsible for total thickness but their determination are perchance not encountered for three components system. In this context, we have performed molecular dynamics (MD) simulations of a technologically important water–dodecane system containing tri-isoamyl phosphate (TiAP) used for reprocessing of radionuclide. MD simulations provide a microscopic view of the interfacial properties of water–dodecane/TiAP interface. Further, an empirical relation between interfacial tension and interface thickness has been established for water–dodecane/TiAP system [1] (see inset of Fig. 1) which is also related by capillary wave theory (CWT) as:

$$w_c^2 = \frac{k_B T}{2\pi\gamma} \ln \left( \frac{L_{II}}{L_b} \right)$$

Here,  $k_B$  is Boltzmann constant and  $T$  is temperature,  $L_{II}$  is the box dimension along  $x$  or  $y$  direction.  $L_b$  represents bulk correlation length commonly expressed in terms of molecular length which is evaluated from the volume determined by COSMOtherm program at the BP/TZVP level of theory as implemented in Turbomole package. The calculated  $w_c$  for water–dodecane system [1] (0.202 nm) is in good agreement with reported (0.338nm) results [2]. For a three components system, it is reasonable to introduce the weighted average of dodecane and TiAP for determination of Lb to account the effect of TiAP. Furthermore, the total interface thickness ( $w_t$ ) cannot be solely represented by  $w_c$ . The wt can be empirically fitted as [1]:

$$w_t^2 = \frac{(\sigma_{water} + \sigma_{TiAP} + \sigma_{dodecane})}{1.4\sigma_{water}} \frac{k_B T}{\gamma} \ln \left( \frac{L_{II}}{L_b} \right)$$

The total interface thickness obtained from density curve and Eq. (2) are in good agreement as shown in Fig. 1 as a function of mole fraction of TiAP and acid concentration. Eq. (2) might be useful for determining  $w_t$  for a wide range of bi-phasic system.



$W_t$  from density curve and Eq. (2) as a function of (a) mole fraction and (b) aqueous phase acidity.  $W_c$  and vs. mole fraction of TiAP [inset of Fig. (a)]

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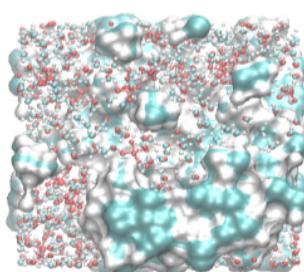
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# Mechanism of Hydroxide Ion Transfer through Anion Exchange Membrane in Anion Exchange Membrane Fuel Cell: Investigation using Molecular Dynamics Simulation

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Anion exchange membrane fuel cells (AEMFCs) have great potential over proton exchange membrane fuel cells (PEMFCs) due to cost-effective energy conversion. However,  $OH^-$  ion transport is a key obstacle. It is evident that  $OH^{-1}$  ion can move through the hydrated AEM via two ways: (i) Grotthuss mechanism either via water chain or via AEM membrane surface sites, and (ii) Vehicular diffusion via Brownian motion. A recent study based on multistate empirical valence bond (MS-EVB) by Chen et al. has proposed that the vehicular diffusion contributes approximately 80% to the total diffusion of the hydroxide ion via the hydrated poly-vinyl benzyltrimethylammonium (PVBTMA) polymer. The remaining 20% is contributed by the Grotthuss mechanism. This striking importance on vehicular diffusion motivated us to focus on the vehicular diffusion of the hydroxide ions. In addition, a couple of more recent studies have demonstrated a much larger importance of Grotthuss diffusion over the vehicular diffusion of hydroxide ion in a different AEM. Thus there is a need for more investigation to understand the  $OH^{-1}$  ion transport. In this work, we used empirical force-field based classical MD simulation to understand the structure and vehicular diffusion of  $OH^{-1}$  ion. However, this method is inadequate to explain reactions or transformations where bond breaking and formation occurs. But the vehicular diffusion is obtained here in a straightforward way. This gives us a better understanding of the possible role of  $OH^{-1}$  ion transport via vehicular diffusion; results will be discussed in the poster in more detail.



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# Water-Mediated Curvature Change in Graphene by Single-Walled Carbon Nanotube: A Molecular Dynamics Study

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Novel nanostructured materials possessing new architectural segments can be synthesized using the various combinations of graphenes and carbon nanotubes (CNT) that can result into the generation of enhanced physico-chemical properties within the hybrids. Comprehending the various physical processes involved in the creation of these new segments is crucial for designing an optimized nanomaterial for a specific purpose. In this work we report induced folding in a graphene sheet resulting from the physical interactions between a water-mediated graphene and a CNT. Owing to robust binding interactions between the CNT and a compatible graphene sheet, the latter forms a second domed layer around the former culminating in a structure equivalent to a double-walled CNT. The induced curvature change in graphene by CNT was found to have strong dependencies upon their relative physical dimensions. For example, CNT possessing extreme small diameters are unable to induce any significant curvature changes in longer graphene sheets. The potential-of-mean force (PMF) between our reference graphene and CNT in water suggests a favorable binding interaction of 14.5 kcal mol<sup>-1</sup>. The breakdown of PMF into direct graphene-nanotube interactions and water-mediated interactions reveals huge reduction in the strongly attractive binding interactions between graphene and CNT by the water molecules.



Potential-of-mean force for pulling center of mass of graphene from the bulk water on the outer surface of CNT along the x-axis.

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# **Characterization of Biological Water at Interface of Antimicrobial Peptide in Presence of Salts Solution**

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Alkali metal ions are known to play an important role in stabilizing proteins by changing its hydration environment. Water molecules around the hydrophobic and hydrophilic sites of protein molecules are important as effect the structural and dynamics properties Hu and Jiang (2008). Molecular dynamic simulations of an antimicrobial peptide (AMP) [PDB ID: 5Z32, Mohid et al. (2019)] was carried out in presence of 0M and 0.25M salt (NaCl, KCl, LiCl) solutions in aqueous medium to characterise the interfacial water at its hydrophobic, hydrophilic and mixed region. We present here the radial distribution function (RDF), orientation profile, local structure parameter, diffusion and excess entropy of water to assess its structural and dynamics properties at the interface and bulk regions. RDF's of C-Ow showed higher hydration shell in presence of Li<sup>+</sup>, Na<sup>+</sup> and a broad peak in K<sup>+</sup>. The ions-water RDF shows stronger hydration shell in the presence of Li<sup>+</sup>, Na<sup>+</sup> Hess and van der Vegt (2009). The density of water is found to be smaller in the presence of K<sup>+</sup> as compare to Li<sup>+</sup>, Na<sup>+</sup>. The diffusion coefficient of water molecules is found to be greater in case of K<sup>+</sup> as compared to Na<sup>+</sup> and Li<sup>+</sup> ions. Furthermore, the distribution of the O-O-O angle of water at first solvation shell around ALA2, ARG18 and LEU11 shifted to a higher value in presence of Li<sup>+</sup> than Na<sup>+</sup>, K<sup>+</sup>. The probability of occurrence of higher coordinated water in bulk is found to be more compared to the first and second hydration shells. The calculated excess entropy [Yan et al. (2008)] from RDF's shows less value for Li<sup>+</sup> compare to Na<sup>+</sup> and K<sup>+</sup>. Water molecules around the ARG18 shows more tetrahedral order compared to the hydrophobic part of AMP indicating the presence of low density water near hydrophilic region.

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## **Investigation of Cholesterol Influence in Fluid Phase and Gel Phase Lipid Bilayers by Coarse-Grained Molecular Dynamic Simulation**

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Cholesterol plays an important role to regulate various functions of the cell membrane. It is the interaction of cholesterol with lipids that influences the phase state behavior of the lipid bilayer (fluid phase and gel phase) and hence the cellular functions. Therefore, investigation on lipid-cholesterol interaction is of utmost importance. We have carried out a coarse-grained molecular dynamics simulation to understand the cholesterol influence and the phase state behavior. We chose four different lipid bilayers (DOPC, DLPC, DPPC, DSPC) and varied the cholesterol concentration. MD simulations were carried out for 12us, at constant temperature 300k and pressure 1bar using Berendsen thermostat and Barostat respectively.

The obtained results were analyzed and found to have a strong influence on cholesterol but is different for the gel phase and fluid phase. Some of the properties were analyzed are thickness, Area per lipid, Mean square displacement and Radial distribution function. It was found that thickness of the bilayer estimated after simulation is increasing with cholesterol addition by  $\approx 5\%$  for fluid phase and a decrease by  $\approx 7\%$  for gel phase. Whereas, APL found to have an overall decreasing trend by 10%. At higher percentage of cholesterol, Ld phase changes to Lo phase, whereas So phase changes to Lo phase.

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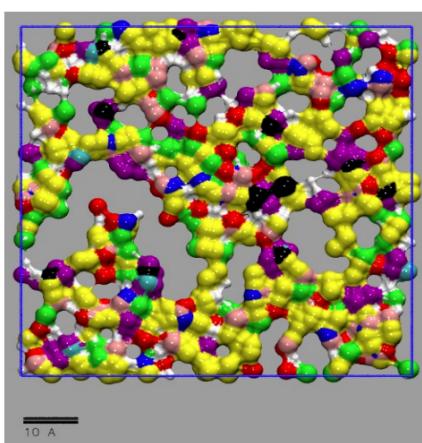
# Microscopic Structure and $CO_2$ Adsorption Properties of 6FDA/BPDA-DAM Polymeric Membrane

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Polymeric membranes are widely accepted as good alternatives for  $CO_2$  adsorption from flue gas, as the process is easy to handle and environmentally friendly. Carbon Molecular Sieve (CMS) membranes are obtained via pyrolysis of such polymeric membranes, which also show high solubility, permeability, and selectivity towards  $CO_2$  molecules [1]. In the case of 6FDA/BPDA-DAM polymer membrane, the cause of high perm-selectivity towards  $CO_2$  is attributed to a rich distribution of ultra-micropores and micropores. To understand the underlying statistics of the pores and their effects on the  $CO_2$  adsorption process, an all-atom Dreiding [2] based force-field is prepared to model this polymer. The force-field is parameterized with the help of dihedral scans. A compression-decompression step, followed by repeated annealing steps are performed using molecular dynamics methods, to obtain the optimum density at room temperature and pressure. The glass transition temperature and porosity of the polymer are also calculated, which matched well with the experimental values. The atomistic distribution along the wall of the pores is calculated using an analytical free-volume calculation method [3]. The pore-size distribution is also calculated, which showed a bi-modal distribution. The solubility of the  $CO_2$  molecules inside the polymer matrix is calculated using grand canonical Monte Carlo methods, which showed a high affinity towards  $CO_2$  molecules. The swelling effects are also studied using a coupled NPT/NVT method. The derived CMS membrane is prepared as a random distribution of pyrrole and pyridine rings [4]. After equilibration, pore-size distribution and  $CO_2$  adsorption properties of this CMS membrane are investigated.



**Figure 1:** A slice of the equilibrated polymer matrix (XY plane) showing various pores.



**Figure 2:** A slice of the equilibrated polymer matrix (XY plane) upon  $CO_2$  (Oxygen – Pink, Carbon – Gray ) adsorption and swelling.

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# Melting in Two-Dimensional Gay-Berne Liquid Crystals

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It is well established that the melting of two dimensional (2D) crystals take place through the unbinding of defects, namely dislocations and disclinations. However, when the constituent particles are aspherical in shape then there are other types of defects appear in the system due to the particles' orientational property, as for aspherical particles, configuration is not only defined by their positions but also by their orientation in space. Systems made up of these particles, show liquid-crystalline phases. In this work, we have performed molecular dynamics simulations of such systems where the interaction between the constituent particles is governed by the Gay-Berne potential such that the particles themselves are like soft ellipses in 2D. We looked at the equilibrium structure by varying densities and temperature of the system. We have used Voronoi construction to identify the distribution of different types of defects in the system and then identified specific temperature and densities at which the system melts from ordered phases (like smectic, nematic) to disordered liquid phase.

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# Molecular Modeling of Phase Equilibrium of Gas Hydrates

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Clathrate hydrates (or gas hydrates) are inclusion compounds in which the host crystal lattice is made up of water molecules connected to each other in a tetrahedral manner via hydrogen bonds. The water lattice contains cavities which are occupied by guest molecules such as methane, ethane, etc. Traditionally, thermodynamics of gas hydrates is described by van der Waals and Platteeuw (vdWP) theory [1] which models the clathrate hydrate as an adsorbent and the cavities as adsorption sites. In this theory, the host lattice is assumed to be rigid. The guest-water potential parameters and empty hydrate properties are usually regressed from experimental phase equilibrium data. Chialvo et al. [2] suggested that the success of the vdWP theory is due to presence of large number of adjustable parameters used in the regression of equilibrium data and the theory acts as a data correlator. Punnathanam and co-workers [3,4,5] showed that the rigid host lattice approximation is a significant source of error to predict the phase equilibrium and developed a method to compute the contribution of movement of water molecules to the partition function, thereby successfully demonstrated the accuracy of the modified vdWP (vdWP-FL) theory using the phase equilibrium data computed using molecular simulations. Later we applied the vdWP-FL theory to model the experimental phase equilibrium data to recompute the guest-water potentials and empty hydrate reference properties are computed directly from simulations. In this implementation of the vdWP-FL theory only one parameter per guest molecule per cage is regressed from experimental data on gas hydrates. The vdWP-FL6 theory gives accurate predictions of the dissociation temperatures and pressures of gas hydrates and their mixtures. In addition, it also predicts the hydrate cage occupancy accurately. Semi-clathrate hydrates are a class of gas hydrates which are also known as ionic clathrate hydrates. In the crystal structure of semi-clathrate hydrates, the water molecules together with anions/cations, by means of hydrogen bonding, form a waterion polyhedral framework. Clathrate hydrates encaging gas molecules are stable only under high pressure and low temperature. On the other hand, semi-clathrate hydrates are stable even at atmospheric pressure. In this work, the phase equilibrium of TBAB semi-clathrate hydrate in its solution is computed using molecular simulations. On the one hand, the aim of this work is to test the accuracy of the selected potential models in predicting the experimental phase equilibrium data.

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## Uncovering the Molecular Mechanism of Solvent-Induced Polymorphism in Crystal Nucleation from Solution

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Crystal nucleation from solution is of great scientific and technological interest in pharmaceutical, chemical and food processing industries. Understanding the role of solvent towards polymorph formation from solution is an important aspect of these studies. Due to the technical limitations of experimental studies, molecular simulations have become an attractive tool for uncovering the molecular mechanisms involved in crystal nucleation. Over the years people have developed specialized molecular simulation techniques to study rare events and applied it to nucleation from melt. The key difference between the nucleation from melt and nucleation from solution is slow diffusion of solute molecules from solution to the surface of the nucleus. As a result, novel strategies are necessary to handle the slow diffusion of solute molecules.

We proposed a method that is based on the molecular theory of nucleation developed by Reiss and co-workers to crystal nucleation. We apply the developed technique to study two systems, nucleation of LJ solid from the vapor phase and crystal nucleation of Orcinol from its solution. Orcinol offers a simple but representative system to study the phenomenon of solvent-induced crystal polymorphism in organic molecular solids. Though orcinol has many polymorphs, pseudo polymorphs, solvates and hydrates in different solvent conditons, we specifically study the crystal nucleation of anhydrous polymorphs of Orcinol from solutions. Our simulations reveal the role of solvents towards polymorph selection during crystal nucleation of orcinol and incase of LJ system, free energy profile shows a two step nucleation with only one saddle point.

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# A Functional Force Field Model for Water Based on Gaussian Charges

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At a molecular level, even though water is a simple three atom molecule, its behavior in bulk is quite interesting and complex. [1] Over the past 60 years, a myriad of point-charge non-polarizable water models have been developed. [2, 3, 4, 5, 6, 7] Although these non-polarizable water models are simple and computationally efficient, none of them satisfactorily predicts all the properties of water. [8] For much higher accuracy polarizable water models are used which require much greater computational power. Therefore, there is a need to develop accurate, simple and computationally efficient empirical models which can be used for large- scale simulation of large systems like electrical double layer.

In this work, we developed a novel 4-site, rigid, Gaussian charge water model, by a two-step fitting process. a) The Gaussian sizes and charges are fitted to get the positions and magnitude of critical points in the gas-phase electrostatic potential and the dipole moment of water. b) The parameters for non-bonded interactions are fitted to interaction potential of water-water in several key configurations in gas-phase obtained from accurate quantum chemical calculations.

Further the model is tested for water clusters from (trimer to hexamer). We also developed a simulated annealing code to obtain guess configurations for different water clusters. The energies for these clusters were finally compared with CCSD (t)/CBS model chemistry. Qualitatively, our model predicts the stable configurations of trimer, tetramer and hexamer correctly, but fails in the case of pentamers. We are currently in the stage of re-parameterizing the model to eliminate discrepancies.

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## A Temperature Accelerated Sliced Sampling Study on Drug Binding/Unbinding

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Molecular dynamics simulations using enhanced sampling techniques are widely used to explore the rugged free energy landscapes of drug binding/unbinding in proteins. Collective variable based techniques for enhanced sampling have severe drawback that their free energy convergence is slow when the dimensionality of the landscape goes beyond two or three [1]. Sampling of large number of transverse coordinates are vital to obtain reliable free energy estimates and quick convergence. Along the extent of the reaction, the essential transverse coordinates for sampling may change. Moreover, a controlled biased sampling is essential to overcome the “leak out” of biasing energies. Recently, we proposed a novel sampling technique called “Temperature Accelerated Sliced Sampling” (TASS) to overcome these limitations [1-3]. In this work, we demonstrate the application of the method in modelling binding/unbinding reaction pathways of avibactam, an FDA approved -lactamase inhibitor, with Class-C  $\beta$ -lactamase [4].

Based on this study we obtain full atomistic details of the binding/unbinding reactions, the intermediate steps thereof, critical interactions and free energetics. We illustrate how TASS method could aid in exploring high dimensional free energy landscapes when large number of collective variables are required, and different transverse collective coordinates are taken for different slices. Of great interest, we observe that ligand solvation/desolvation is a vital collective variable for obtaining correct free energetics of drug binding/unbinding.

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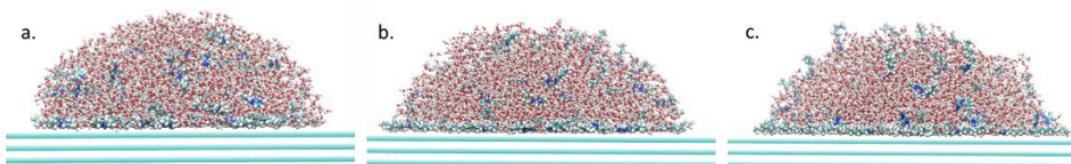
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# **Effect of Alkyl chain on The Wetting Behavior of Aqueous Ionic Liquids: A Molecular Dynamics Study**

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We report a Molecular Dynamics investigation on the effect of alkyl chain on wetting and interfacial properties of aqueous imidazolium-based ionic liquids (ILs), consisting 1-ethyl-3-methylimidazolium [EMIM], 1-butyl-3-methylimidazolium, [BMIM] and 1-Hexyl-3-methylimidazolium [HMIM] cations with common tetra fluoroborate anion. Effect of alkyl chain length on wetting behavior of aqueous IL within concentration range of 10~30 wt% IL were studied (Figure 1). The difference between the contact angle for aqueous [EMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] droplets are small, irrespective of wt% of IL. However, drastic decrease in the contact angle was observed for long alkyl chain [HMIM][BF<sub>4</sub>]. Droplet characteristics near the surface were investigated by profiling the density perpendicular (z-direction) and horizontal (r-direction) to the graphite sheet; which was further quantified by an orientation order parameter. Most of IL molecules are found near the graphite surface for all the cases. However, presence of longer alkyl [HMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] are found in the liquid-vapor interface, which are in agreement with the literature<sup>1–3</sup> which deals with aqueous solutions of IL at solution/vapor interface. Further, hydrogen bond analysis between IL and water at different wt% are also investigated. Chain length of cation, and interfacial tensions of aqueous ILs which has been compared with the experimental values [4,5] are the crucial factors for wetting behavior of aqueous IL in our study. In addition to that, we have also investigate the electrowetting behavior of ionic liquid droplet at different strengths of electric field.



**Figure 1:** Snapshot of 30 wt% of aqueous a) [EMIM][BF<sub>4</sub>] b) [BMIM][BF<sub>4</sub>] c) [HMIM][BF<sub>4</sub>]

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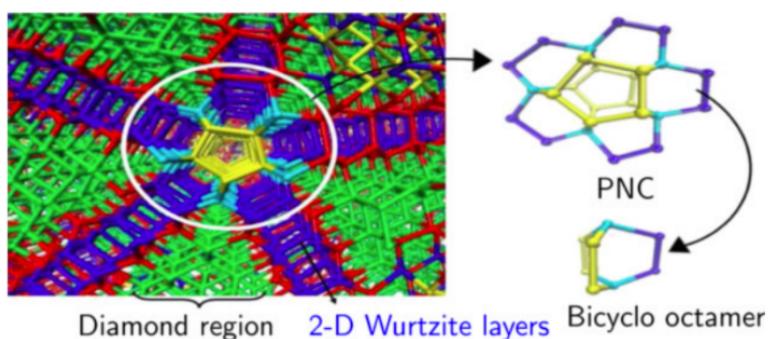
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# Topological Identification Criteria, Stability and Relevance of Pentagonal Nanochannel in Amorphous Ice

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The fivefold symmetric structure is commonly found in nature [1] and in different class of materials such as metallic glasses, [2] metal-alloys, [3] nanocrystalline materials, [4] and hard-sphere systems, [5]. Considering the potential importance of pentagonal nanochannels (PNCs) in determining the structure of the amorphous ice, we introduce topological criteria to identify the PNCs with an optimal fivefold symmetric environment. The basic building block in our criteria (see Figure1), termed as a bicyclo octamer, is an axisymmetric cluster formed by combination of three six-membered boat-shaped rings. The shape of boat and chair rings identify using dihedral angle criteria. [6] This bicyclo octamer unit serves as a seamless interface of the PNCs with cubic-hexagonal stacking patterns of the amorphous ice. This interface results in a fivefold symmetric mesostructure of relatively high stability: a central PNC with extended five branches of two-dimensional (2-D) hexagonal (wurtzite) crystalline monolayers stacked with cubic (diamond) layers. We also unearth a hierarchy of symmetric structures in amorphous ice: the PNCs, together with dodecahedron cages, form a network consisting of (nearly) equilateral triangular patterns. At the next hierarchical level of symmetry, such triangular patterns combine to form triangular pyramids with dodecahedron cages as the vertices, PNCs as the edges, and confined 2-D hexagonal crystalline monolayers as the triangular faces of the pyramids. The central core of the pyramids consists of cubic (diamond) regions with a strong local tetrahedral order. The overall structure of the amorphous ice states is found to be profoundly affected by PNCs. Specifically, in states with a relatively large number of PNCs, the cubic- hexagonal stacking is primarily in the form of hexagonal crystalline monolayers stacked from both sides with cubic crystalline layers [7].



**Figure 1:** Basic building block to identify the pentagonal nanochannel (PNC).

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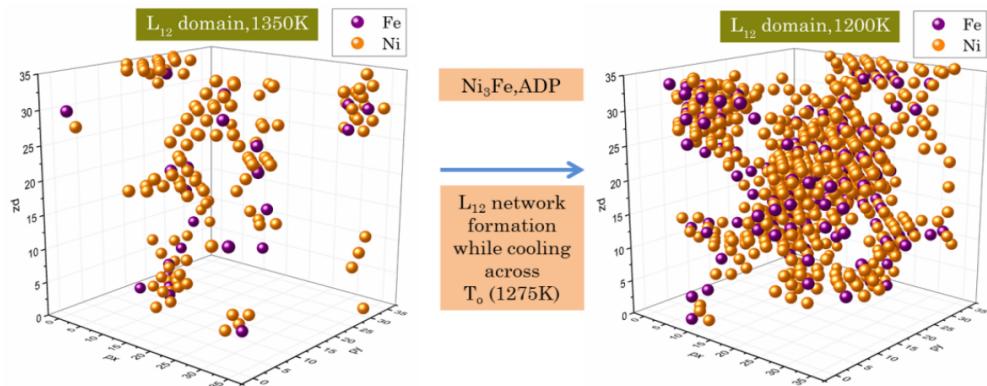
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# A Thermodynamic Perspective of Order-Disorder Transition of $Ni_3Fe$

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The order-disorder (OD) transition temperature of  $Ni_3Fe$  ( $\approx 779\text{ K}$ ) is well known from several experimental investigations primarily based on Mossbauer spectroscopy (MS) and electrical resistivity measurements [1,2]. Across  $T_O$ ,  $Ni_3Fe$  undergoes a transition from a disordered solid solution with a FCC structure to an ordered intermetallic compound with a  $L_{12}$  structure (in which Fe atoms are at the corners and Ni atoms are at the face centers of the FCC lattice). Here we investigate the mechanism of the transition with molecular simulations using two potentials based on embedded atom method (EAM). One of the EAM potentials includes angular dependent terms which are considered crucial in case of Fe based alloys. Although the OD transition temperatures are higher than the actual value, the alloys simulated using both the potentials show qualitatively similar mechanism. As the alloy is cooled from the disordered state to the transition temperature  $T_O$ , there is a large increase in Fe and Ni atoms with  $L_{12}$  local order that does not exceed beyond third coordination shell. There is a significant change in the bulk density and the long range order parameter (LROP), which increases from 0 in the disordered state to about 0.85 at  $T_O$ . However the size of the  $L_{12}$  ordered domains and hence the  $L_{12}$  global order does not increase significantly. Across  $T_O$ ,  $L_{12}$  ordered domains gain critical strength to overcome thermal fluctuations. This is supported by the fact that the number of bulk sites of the  $L_{12}$  ordered domains exhibit an inflection at  $T_O$  and increase relatively rapidly as the temperature is reduced below  $T_O$ . We find that the mechanism is similar to that of crystallization across the limit of stability of super cooled tetrahedral liquids such as silicon and water [3]. Such a mechanism, as found by earlier simulation studies, involves freezing of the tetrahedral network (against thermal fluctuations) followed by rapid growth of the network as the temperature is reduced across the stability limit. Our results indicate that OD transition temperature  $T_O$  in the actual  $Ni_3Fe$  alloy, from a thermodynamic perspective, is possibly lower than the temperature across which sharp changes (due to  $L_{12}$  local order) are observed in the LROP as well as in the bulk density.



**Figure 1:** On cooling,  $L_{12}$  domain (global  $Ni_3Fe$  order) increases steeply across transition temperature ( $T_O$ ). Above figure is generated using ADP force field for  $Ni_3Fe$  system.

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# **Understanding the Adsorption Mechanism of Arsenous Acid on Magnetite (311) Surface through Molecular Dynamics Simulations**

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Adsorption is the favored technique for the removal of toxic arsenous acid ( $\text{As(OH)}_3$ ) from groundwater. The method can be made more economically workable by the utilization of attractively magnetic recyclable adsorbents. There are few reports on the successful use of magnetite as an adsorbent of arsenous acid. However, none of researcher attempt to give any systematic understanding into the molecular-level interactions between the magnetite surface and arsenous acid in the presence of water molecules. Understanding the mechanism involved is critical for the development of better adsorbents of  $\text{As(OH)}_3$ . In this work, we studied this issue by employing classical molecular dynamics simulations for adsorption of arsenous acid in the water on the magnetite (311) surface. Long-time radial distribution function analysis tells the two interactions (1) Fe (of magnetite) and O (of arsenous acid) and (2) O (of magnetite) and H (of arsenous acid) dominate the adsorption interactions at the molecular level. The adsorption isotherm and equilibrium constant have also been calculated and reported.

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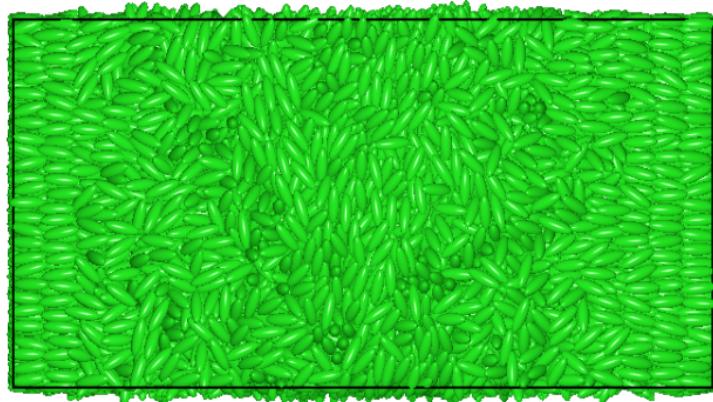
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# Temperature Dependent Interaction of Soft Repulsive Wall with the Thermotropic Liquid Crystals

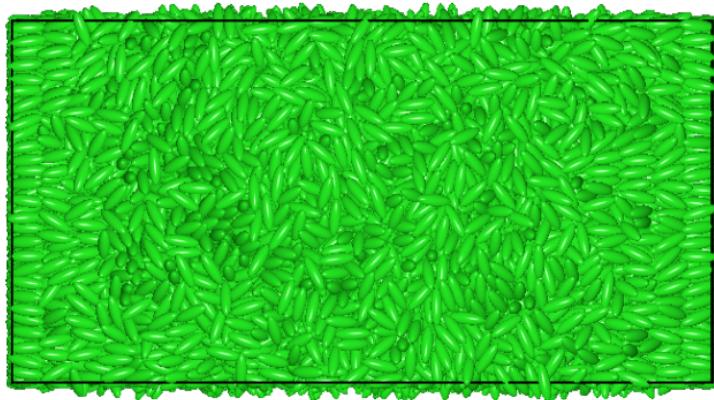
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Using computer simulations, the effect of soft repulsive wall on a system comprising of thermotropic liquid crystalline material is studied. We place the walls perpendicular to the z-axis at the ends of an anisotropic box with the periodic boundary conditions along x and y axes. Here, the wall interaction strength, temperature and density are the control parameters. We analyzed the effect of temperature on the system confined by the wall at different number densities. Within a limited range of temperatures, we observe that temperature is actually a good control parameter in the system. Moreover, the effect of wall on the system is more pronounced at low number densities. Below are the snapshots of wetting of walls with the bulk liquid crystalline phases at the same density and at two temperatures with  $T = 0.8$  (left side) and  $T = 1.0$  (right side).



**Figure 1:** At  $T = 0.8$  and  $\rho = 0.3137$ , the bulk (center of the box) phase is the isotropic liquid but the order of the particles away from bulk and close the walls are changed and observed to form layers parallel to the walls.



**Figure 2:** At  $T = 1.0$  and  $\rho = 0.3137$ , the bulk (center of the box) phase is the isotropic liquid but the order of the particles away from bulk and close the walls are changed and observed to form layers parallel to the walls. Here the number of layers formed near the wall is less than that of  $T = 0.8$ .

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# **A Comparative Study of Tackifying Monomers to Develop Bio-Based Pressure–Sensitive Adhesive: A Computational Approach**

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The demand of pressure sensitive adhesives (PSAs) has grown very rapidly in food packaging, stationary and healthcare industries owing to its characteristic adhesion property. Several petro- based tackifying monomers such as 2-ethylhexyl acrylate (2-EHA), iso-octyl acrylate and n-butyl acrylate provide sufficient substrate adhesion but these are neither sustainable nor renewable. The bio-sourced acrylated epoxidized linseed oil (AELO) and acrylated epoxidized methyl ester (AEME) have the potential to act as tackifying monomer which are renewable, sustainable, cost effective and ecofriendly in nature. In this investigation, molecular dynamic (MD) simulations have been employed to estimate their surface energy and binding energy against aluminum substrate. Further, mechanical response (shear and bulk modulus) was investigated to understand their resistance ability against shear deformation. The fractional free volume was estimated by varying applied stress and temperature, and further used to investigate their viscoelastic behavior to understand the ease of processability and compatibility. Besides being renewable and sustainable, both AELO and AEME showed improved surface energy, substrate binding energy, shear and bulk modulus, in comparison to chemically sourced 2-EHA. Moreover, AEME showed better performance properties than AELO, and thereby, proposed as a potential green tackifying monomer for developing PSAs.

# **Oil Detachment from Rock Surface using Nanoparticle, Surfactant and Low Salinity Brine: A Molecular Dynamic Study**

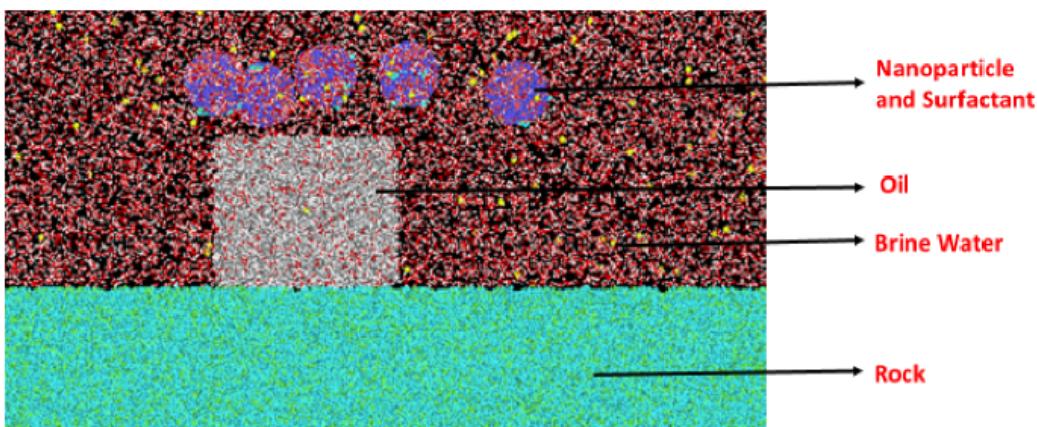
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Chemical enhanced oil recovery (EOR) is a promising method to meet the continuous increase in oil demand and keep sustainable oil supply [1]. Nanomaterials, surfactants and ions have received major attention due to their potential application in EOR[2]. The main function of these materials is to help in wettability alteration, reduces interfacial tension, increasing viscosity of water, self-cleansing agent, etc. which finally results in destabilizing the oil layer at rock surface causing easy oil recovery[3].

We investigated the oil detachment mechanism from the sandstone surface using nanoparticle, brine water of low concentration and surfactant using molecular dynamic simulation as shown in Fig.1. Through analysis of all ionic, atomic and molecular force field and surface interaction between rock -fluid were done at reservoir operating conditions. The result showed that both surfactant and nanoparticle are adsorbed at oil and brine interface which reduces the interfacial tension and increases the total surface pressure resulting in oil detachment. Synergistic effect of ionic species, surfactant and nanoparticles on wettability alteration of rock surface from oil-wet to water-wet condition were also investigated. Our molecular simulation study provided information on the oil detachment from the rock surface. This is useful for petroleum industries to understand the underlying mechanism of complex injecting fluid for optimal oil recovery which will play a major role in future oil supply.



Simulation model schematic diagram

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## High Throughput Screening of Hypothetical Metal Organic Frameworks for Ethane – Ethylene Separation

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Ethylene ( $C_2H_4$ ) is the largest feedstock in petrochemical industries, and it is produced by thermal decomposition of ethane ( $C_2H_6$ ), in which a certain amount of  $C_2H_6$  residue coexists in the product and needs to be separated to produce polymer-grade  $C_2H_4$  as the feedstock for many other products, particularly the widely utilized polyethylene. The well-established industrial separation process of ethylene from ethane is cryogenic distillation, which is one of the most energy-intensive processes in the chemical industry because of the similar volatilities and sizes [1]. Hence, there is a need to find an alternative technique to minimize energy consumption. Among the technologies recently developed, adsorbent-based gas separation through pressure swing adsorption (PSA), temperature swing adsorption, or membranes is a promising technology. Currently, the database of experimentally discovered MOFs is in millions, and it is growing yearly. Hence, a hybrid approach combining machine learning algorithms with molecular simulation is necessary.

In this work, we screened the hypothetical Metal Organic Frameworks (h-MOF) database [2] using the molecular simulation coupled with Random Forest [3] (RF) regression algorithm. In particular, we rationalized the relation between structural and chemical properties of h-MOF with the  $C_2H_6$  /  $C_2H_4$  selectivity. The database consists of 137,953 hypothetical MOFs. As chemical, and structural properties are often correlated with the adsorption capacity, we calculated several structural and chemical descriptors in order to leverage the accuracy of the machine learning model. 8% h-MOFs were chosen randomly from the h-MOF dataset as a training set, and simulated at 298 K, and 1 bar, by using multi-component grand-canonical Monte Carlo (GCMC) algorithm to get the equilibrium  $C_2H_6$  /  $C_2H_4$  selectivity. Based on the training set the RF model was developed with 250 trees. We got 35

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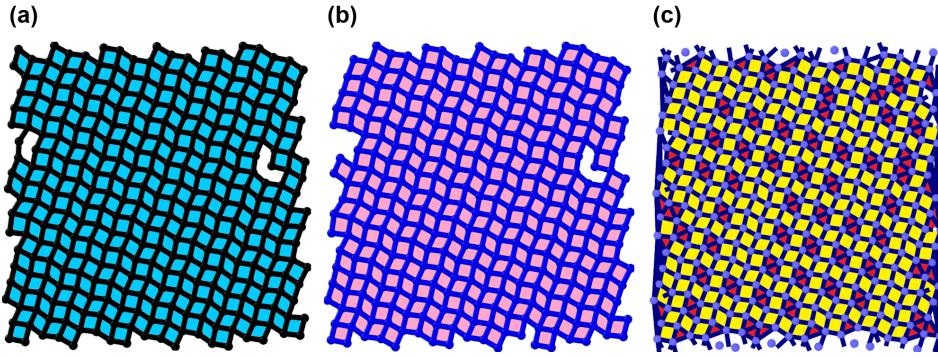
# **Formulation and Implementation of General Topological Network Criteria for Exploring the Structures of Confined Ice**

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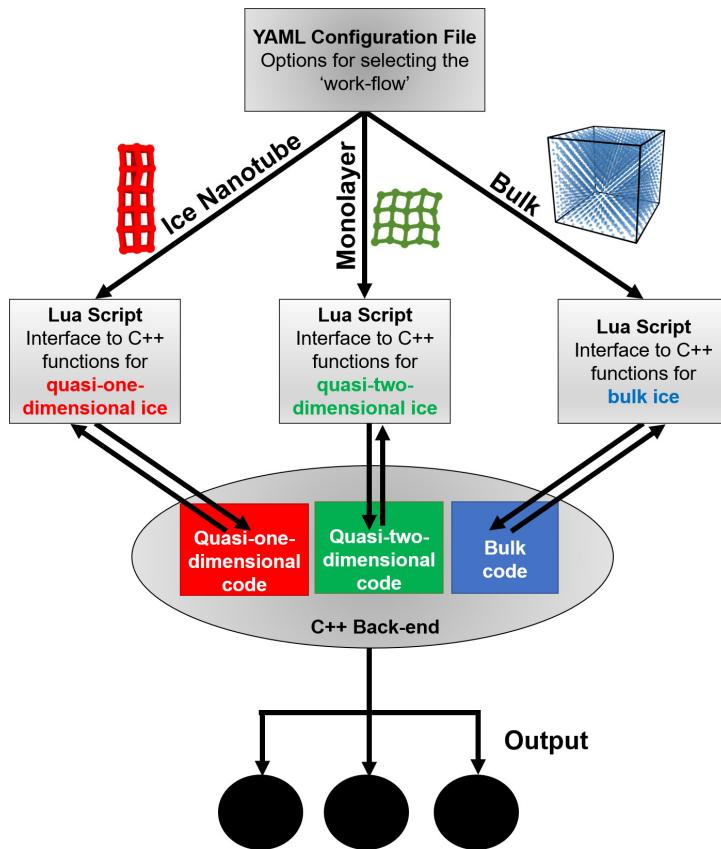
We present a family of general topological criteria, for the determination of structures of quasi-one-dimensional and quasi-two-dimensional ices [1]. Confined systems are characterized by a plethora of diverse ordered structures and interesting hydrogen-bond-networks (HBNs), distinct from those formed in the bulk. Our methodology has no a-priori assumptions, and can be used as an exploratory tool for probing confined ice structures. In our recipe, primitive rings are identified, and further, only connections corresponding to hydrogen bonds are permitted. Figure 1 compares the accuracy of our methodology with that of Voronoi tessellation, for flat Monolayer Square Ice (fMSI). The prism identification scheme developed identifies prismatic units, which are the building blocks of ice nanotubes (INTs). In addition, we formulate novel and intuitive order parameters based on our topological network criteria, which are able to qualitatively and accurately describe phase transitions.

We have subsumed this new methodology, along with other popular structure determination algorithms, into a framework developed for the analysis of molecular simulations. We present d-SEAMS (deferred Structural Elucidation Analysis of Molecular Simulations), a free and open-source post-processing engine [2]. The software automates the classification of ice structures for both confined and bulk ice for the first time. The framework of d-SEAMS is also unique, and designed to ensure reproducible research and easy extensions, without compromising functionality. D-SEAMS uses nix [3] for generating a reproducible and deterministic dependency build-graph, thus circumventing package dependency clashes [4]. A YAML-Lua scripting interface enables users to interact with the C++ backend. Figure 2 shows the work-flow implemented in d-SEAMS. Key features implemented include topological network criteria for bulk and confined ice, ring statistics, intuitive geometric order parameters and bond-orientational parameters. The outputs produced by d-SEAMS are consumable by popular graphics software suites, for immediate visual insights into the systems studied.



**Figure 1:**

Comparison of the accuracy of Voronoi tessellation with our topological network criterion for identifying fMSI. fMSI is known to consist of 4-membered polygons. (a) The top view of the HBN, with 4-membered polygons shaded in cyan. Identification schemes should closely approximate the HBN connectivity. (b) The ring network generated by our topological network criterion, with 4-membered rings shaded in pink. (c) Neighbour bonds created by Voronoi tessellation. The bonds (in black) are generated by connecting neighbouring particles (blue) which share a Voronoi face. Polygons thus formed, with three and four edges, are coloured in red and yellow, respectively. The Voronoi cells are 5-membered and 4-membered polygons, depending on the coordination number.



**Figure 2:** Code pipeline of d-SEAMS. The YAML script file provides options to choose the type of the system and

the corresponding work-flow, for either bulk, quasi-one-dimensional quasi-tqo-dimensional monolayer sytems. The Lua interface functions interact with the C++ functions for each work-flow, and functions of other work-flows are not exposed to the user.

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