ChemE In-house Symposium

February 18, 2017

Department of Chemical Engineering

Indian Institute of Science, Bangalore

WELCOME

On behalf of the members of the Chemical Engineering Association (CEA), Indian Institute of Science, Bangalore, I extend a warm welcome to all the participants of the 2017 edition of the Annual Chemical Engineering @ IISc Symposium (CIS 2017).

This symposium is one in a long series of annual symposiums that is organized by the CEA with the help of the Department of Chemical Engineering to primarily highlight the research pursued by the students of the department. Our students work on a diverse set of problems and this year's edition features talks in the areas of rheology, catalysis, biological systems, energy storage and computation molecular science. We also have the honor of having Dr. H. Mary Bastian (Shell) as our distinguished plenary speaker from the industry this year. A member of our faculty, Dr. Bhushan Toley, will present a talk on paper-based microfluidics.

CIS 2017 also follows the footsteps of such previous symposia in the department to help us promote increased interaction with the industry.

We hope the participants will enjoy the symposium and find time to interact with ChemE department members. We thank all the participants and members of the Chemical Engineering Department for taking their time this weekend for attending the symposium and helping us make it a success.

Sudeep Punnathanam
President
Chemical Engineering Association

Technical Program

08:30 – 08:55	**Registration & Coffee**	
08:55 – 09:00	**Chairman's Address**	
	Session I	
09:00 – 09:15	Satyaghosh Maurya	Understanding assembly pathway of biological nano-pore forming toxins
09:15 – 09:30	Bharadwaj Vemparala	Modelling bacterial signalling systems and the effect of crosstalk
09:30 – 09:45	Vadhana V	Towards addressing confinement induced transitions of a Lennard-Jones fluid: a molecular dynamics study
09:45 – 10:00	Shivanand Kumar	Molecular simulation studies on clathrate hydrates
10:00 – 10:15	Ravi Kumar Reddy	Free energy calculations of solids with flexible molecules
10:15 – 11:15	**Coffee & Poster Session I**	
	Session II	
11:15 – 12:00	Dr. Hyacinth Mary Bastian, Team Lead, Shell Technology Center, Bangalore	Energy Transition: Role of long range research @ Shell
12:00 – 12:45	Dr. Bhushan Toley	Increasing global access to medical diagnostic testing using paper-based microfluidics
12:45 – 14:00	**Lunch & Photo Session**	
	Session III	
14:00 – 14:15	Ganesh Madabattula	Self-discharge in electrochemical double layer capacitors
14:15 – 14:30	Md Aslam Ansari	Alternative designs to harness natural convection in flow batteries
14:30 – 14:45	Phanikanth Sanagavarapu	Stress relaxation in a bacterial suspension: The active-to-passive transition
14:45 – 15:00	Sagar Bharatraj	Rheology of dense granular chute flow: Simulations to Experiments
15:00 – 15:15	Peter Varun Dsouza	Secondary flows in sheared granular systems
15:15 – 16:15	**Coffee & Poster Session II**	
	Session IV	
16:15 – 16:30	Satyapaul A. Singh	Role of hydrogen and oxygen activation over Pt and Pd doped composites for catalytic hydrogen combustion
16:30 – 16:45	Neha Lamba	Supercritical transesterification: An approach towards sustainable biodiesel production
16:45 – 17:00	Ravi Kiran M	WGS activity and detailed kinetic modeling of WGS over platinum based bimetallic Ceria
17:00 – 17:15	Rimzhim Gupta	Ag & Cu impregnated Fe doped ZnO for bacterial inactivation under visible light
17:15 – 17:30	**Prizes & Vote of Thanks**	
17:30 – 18:00	**High Tea**	
19:30	**Dinner at Jawahar Guest House, IISc**	

Poster Session I

P1	Amannuel	New physical insights into shear history dependent polymorphism in PVDF
P2	Amit Behera	Using molecular dynamics simulations to understand the role of cholesterol during pore formation in lipid bilayers
P3	Arjun Gopal	Modelling combination therapy of oncolytic viruses with immune checkpoint blockade drugs
P4	Aswin Vinod	Antifreeze proteins – A molecular dynamics study
P5	Bhanjan Debnath	The lift force and the torque on a disc immersed in a rotating granular material
P6	Ch. Anil	Development of ionic substituted manganese oxide catalysts for CO oxidation
P7	Ch. Sai Kumar	Catalytic isomerization in 1-pentene: Density Functional Investigation
P8	Disha Jain	Dry reforming of methane over Ce-pyrochlores
P9	Gokulakrishnan Subramanian	Fenton based advanced oxidation processes for water treatment
P10	Ilanila.I.P	Probing the kinetics of protein-lipid interactions in Giant Unilamellar Vesicles (GUVs)
P11	Jatin Panwar	Suction microfluidics: Architecture and applications.

Poster Session II

P12	Mani Sravani	Study of high mach number turbulent flow in a channel by DSMC simulations
P13	Naveen Kumar	Study of the mechanical behaviour of hair fibre
P14	Nuruddin Bahar	Towards DNA origami-based magnetic nanopropellers
P15	Rajasekaran M	Water adsorption on graphene oxide
P16	Ramkumar	Step towards mimicking biology with DNA origami-graphene hybrid nanopore
P17	Rubesh Raja	Using mathematical models to improve the treatment of hepatitis C virus (HCV) infection
P18	Saurabh Umrao	Characterizing DNA aptamer based biosensors using single molecule spectroscopy and fluorescence lifetime imaging microscopy
P19	Subhasish Baral	Synergy between innate and adaptive immune responses may decide the fate of HCV infection
P20	Suhas Mukherjee	Insights of preferential CO oxidation mechanism over copper substituted cobalt oxide supports
P21	Suraj Jagtap	Self-assembly of M13 bacteriophage

Contents

Understanding assembly pathway of biological nano-pore forming toxins

Satyaghosh Maurya, Pradeep Sathyanarayan[1], Monisha Ravichandran, Sandhya S. Visweswariah[1], K. Ganapathy Ayappa, and Rahul Roy
[1]Center for Biosystems Science and Engineering, IISc Bangalore

Pore-forming toxins (PFTs) expressed by pathogenic bacteria form nanoscale pores on target cell membranes resulting in cell death. Water soluble monomers of ClyA, a representative α-helical PFTs undergo structural rearrangements to a protomer form upon binding to bilayer membrane and further oligomerize to form stable pores. The molecular mechanisms giving rise to selective pore formation on eukaryotic membranes have been unclear, especially in the case of alpha PFTs. Here, we use single particle fluorescence microscopy to examine the events in the pore formation pathway. We demonstrate how cholesterol is a critical component for effective pore formation and a possible means for selective targeting by PFTs. Binding of ClyA, a representative αPFT from *E. coli* on supported lipid bilayers was rapid and complete within seconds. From diffusional and trajectory analysis of single particles, we observe that the monomeric protein transitions between a high and low mobility state via an intermediate. We argue that the lowest mobility ClyA conformation represents a stable membrane bound intermediate along the assembly pathway. This 'immobilization' kinetic is accentuated in bilayers with cholesterol highlighting its role in ClyA pore formation. Dye photo-bleaching and brightness analysis of ClyA oligomers at high concentrations suggests that cholesterol enhances the fraction of oligomers leading to pore formation possibly by stabilizing the assembly intermediates.

Modeling bacterial signaling systems and the effect of crosstalk

Bharadwaj Vemparala, Arjun V. P, and Narendra Dixit

Bacteria sense changes in their environment through two-component signalling (TCS) systems. TCSs contain a trans-membrane histidine kinase (HK) protein and a cytoplasmic response regulator (RR) protein. HK detects a stimulus and gets phosphorylated, it then binds and transfers the phosphoryl group to its cognate RR. Activated RR then trans-locates to the nucleus and triggers gene expression, eliciting responses that are essential for the bacterium to adapt. Though different TCS systems detect distinct stimuli, binding regions of HKs and RRs share significant similarity, pointing towards the possibility of crosstalk between HKs and non-cognate RRs. Studies performed on model organisms like *E. coli* and *C. crescentus* have proven that dissipation of signal flow impairs adaptability. But, interestingly, extensive crosstalk was observed in vitro between the TCS pathways of *M. tuberculosis*. In order to understand this peculiarity, we have modeled and simulated TCS systems. Our results prove that crosstalk patterns mirroring the stimuli sequence confer fitness advantage by priming the organism for upcoming signal. We obtained evidence of this evolutionary advantage using phylogenetic analyses. In summary, our study provides a unique reason for the existence of crosstalk between TCS networks. Blocking crosstalk may prove a novel intervention strategies for bacterial infections.

Towards addressing confinement induced transitions of a Lennard-Jones fluid: a molecular dynamics study

V. Vadhana, Chandan Dasgupta, and K. Ganapathy Ayappa

Molecular dynamics (MD) simulations were carried out for a pure component, monoatomic Lennard-Jones fluid confined between mica surfaces. When the surface separation is an integral multiple of the molecular diameter, the fluid forms distinct layers whereas, jammed layers are formed for intermediate surface separations. The in-plane pair correlation function (PCF) analyzed for contact as well as inner layers begins to exhibit long range translational ordering when the separation distance between the mica surfaces is decreased below four molecular diameters. We also observed a transformation of contact layers from square symmetric structures to a state when square and triangular symmetric structures coexist as the surface separation is decreased below four molecular diameters. The self-intermediate scattering function (SISF) Fs(k, t), a powerful tool to probe molecular dynamics exhibits a gamut of rich dynamics such as distinct two-step relaxation processes indicative of glassy dynamics as predicted by the mode coupling theory (MCT), relaxation processes characterized by jump dynamics and hopping events [1] where MCT scalings break down as well as a striking transition to non-ergodic states characterized by a non-relaxing SISF for specific surface separations even beyond 500 ns. Although a Lennard Jones fluid has no glass transition temperature by itself and can undergo freezing under extreme confinement [2], this study reveals that, confinement introduces new relaxation processes and length scales that a confined LJ fluid is found to exhibit multiple relaxation regimes different from its corresponding bulk counterpart.

References:

1. L. Yelash, P. Virnau, K. Binder and W. Paul, Europhysics Letters, 2012, 98, 28006.
2. K.G. Ayappa and Ratan K. Mishra, J. Phys. Chem. B, 2007, 111 (51), 14299.

Molecular simulation studies on clathrate hydrates

Shivanand Kumar and Sudeep Punnathanam

Clathrate (gas) hydrates are nonstoichiometric crystalline inclusion compounds in which the host lattice is made up of water molecules and guest molecules consists of typically small gas molecules, such as methane, ethane, carbon dioxide, propane, nitrogen, etc. The host lattice consists of a tetrahedrally bonded framework of water molecules via hydrogen bonds and contain cavity like structures. These cavities are occupied by guest molecules which stabilize the hydrate lattice by lowering the chemical potential of water. The thermodynamics of gas hydrates is described by van der Waals and Platteuw (vdWP) theory [1]. According to the original vdWP theory, the hydrogen bonded water lattice is assumed to be rigid. Recent studies [2,3] have shown that the rigid host lattice approximation is incorrect and can lead to significant errors in predicting phase equilibrium. A method to incorporate the effect of flexibility of water lattice into the partition function of gas hydrates was recently developed by Ravipati and Punnathanam [4,5]. Their approach was successfully demonstrated on simulated phase equilibria of various gas hydrates with AARD within 7.69% for dissociation pressures. In this work, we apply the method to experimental data of gas hydrate phase equilbria, and recompute the guest-water potentials. The empty hydrate reference properties are directly computed from molecular simulations. Our implementation regresses at most two parameters per guest molecule using experimental gas hydrate data. Our method is also consistent with the experimental data of ice-water phase equilibira as well as VLE of guest molecules. The gas hydrates chosen for this study are methane, ethane, carbon dioxide (CO_2), propane, iso-butane, and the hydrates formed by their binary mixtures. Methane, ethane, and CO_2 form sI type gas hydrates whereas propane and iso-butane from sII type gas hydrates. We tested our method with three different models of water, namely, TIP4P/Ice, TIP4P/2005, and TIP4P. The forcefield used for methane, ethane, propane and iso-butane is TraPPE-UA and for CO_2 is EPM2. We compare the predictions of our approach with that of CSMGem. Our results indicate that the TIP4P/Ice water model is the most accurate in predicting the experimental phase equilibrium data. The accuracies achieved using our approach in predicting dissociation temperatures and pressures are comparable to those achieved using CSMGem. In addition, our method can also predict the hydrate cage occupancy accurately.

References:

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2. Pimpalgaonkar, H.; Veesam, S. K.; Punnathanam, S. N. Theory of Gas Hydrates: Effect of the Approximation of Rigid Water Lattice. *The Journal of Physical Chemistry B,* 2011, 115, 10018–10026.
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Free energy calculations of solids with flexible molecules

Ravi Kumar Reddy A and Sudeep Punnathanam

Free energy calculations have become an important area of research, since it can play a predictive role in many natural processes such as protein folding, molecular recognition, solvation thermodynamics and polymorphic transitions in solids. Computational studies on phase transitions and phase equilibria depends on the estimation of free energies in different phases. Though the free energy difference between two phases is sufficient to address many problems, absolute free energy is necessary to study polymorphic transitions. Intra molecular conformations of molecules in crystal are responsible for polymorphs. Existing methods for free energy estimation won't consider the flexibility of molecules (intramolecular interactions). We propose a methodology to evaluate the absolute free energy of solids with flexible molecules using Einstein molecule method (EM). The EM method uses the reference as an Einstein crystal (EC) identical to solid of interest, for which free energy can be evaluated numerically using Monte Carlo integration. By constructing a reversible path between solid of interest and EC, we have calculated the absolute free energy of solids. The consistency of these free energy calculations is verified with the thermodynamic integration between two temperatures at constant density.

Energy Transition: Role of long range research @ Shell

Dr. Hyacinth Mary Bastian
Shell Technology Center, Bangalore

The big challenge for the society and for a company like Shell, is to identify economic pathways to provide much more energy than is being supplied today while at the same time significantly reducing carbon dioxide (CO_2) emissions. Energy transition to a low-carbon future involves producing and consuming energy in a different way than is done today. Long range research platform in Shell is aimed at securing Shell's long term competitive position in the future energy landscape and will help building internal capability for the energy transition. This talk aims to share some of the scientific challenges on future energy businesses, chemicals, methane monetization and environmental sustainability due to energy transition.

Increasing global access to medical diagnostic testing using paper-based microfluidics

Dr. Bhushan Toley

The first step in the treatment of any pathological condition is its diagnosis. Currently, most medical diagnostic tests are conducted in centralized labs using bulky and expensive instruments that require trained users to operate. This infrastructure-heavy model of acquiring medical diagnostic information restricts access to proper medical diagnosis for many, especially in the developing world. In this talk, I will present a new vision of medical diagnostic testing in which state-of-the-art diagnostic tests are miniaturized into handheld devices that can be operated by untrained users. I will present proof-of-concept that this can be accomplished by using "paper-based microfluidics" (PµF's). In PµF devices, fluids flow under capillary pressure generated by porous materials, which eliminates the need for bulky pumps to drive fluids. I will present several new power-free valving strategies for PµF devices that enable conducting multiple chemical and fluidic operations automatically. I will conclude by briefly describing some recent work on the development of a fully automatic handheld nucleic acid amplification device that can be operated by an untrained user and can conduct a sensitive medical test at the point-of-care.

Self-Discharge in electrochemical double layer capacitors

Ganesh Madabattula and Sanjeev Kumar

Self-discharge is loss of stored energy when a charge storage device is not in use. Self-discharge in electrochemical double layer capacitors (EDLC) is believed to be caused by unwanted reactions of impurities in electrode/electrolyte and internal leakage resistance. An investigation is carried out in the present work to quantify self-discharge at individual electrodes in an EDLC using both experimental measurements and a transport model. An EDLC with porous carbon electrodes and sulfuric acid as electrolyte was constructed in our lab. Three point measurements were carried out to delineate electrode specific response. The Self-discharge studies involved open-circuit, galvanostatic and potentiostatic measurements. The analysis of experimental data to arrive at self-discharge mechanisms is carried out using Conway's diagnostic techniques. The ambiguities present in identification of self-discharge mechanisms are highlighted.

A transport model for self-discharge is developed using floating/leakage currents, as the existing equivalent circuit models cannot be used to link effect of physical parameters on self-discharge. The model accounts for different cell potential-dependent self-discharge mechanisms at the positive and the negative electrodes. A model assisted analysis of experimental data is in under progress. The present study helps in extending the understanding of self-discharge in EDLCs.

Alternative designs to harness natural convection in flow batteries

Md Aslam Ansari and Sanjeev Kumar

Harvesting of renewable energy requires development of efficient energy storage systems. Rechargeable redox flow batteries offer certain advantages over other forms of energy storage techniques in use, such as lifting of water, compression of air, etc. In a redox flow battery, with electrolyte flowing through the space between two electrodes, electrical energy is stored as chemical energy through reversible reduction-oxidation (redox) electrochemical reactions. Typical applications of large scale storage batteries include load-leveling, load shaving, large backup power, etc. Although some flow battery systems have been scaled up, we are still far from the desired objective---economical batteries with high energy density, high power density, and long cycle life.

Soluble lead redox flow battery (SLRFB) in its class is the least expensive because of the cost of raw materials and no requirement of expensive proton exchange membrane. However, some challenges such as limited cycle life and low energy efficiency have to be overcome before taking it to the next scale. In our research group, we have established through modeling, electrochemical measurements, and flow visualization that natural convection plays a dominant role. We have harnessed it to develop a new mode of operating a closed SLRFB, in which stirring is provided only during short relaxation stages between charge-discharge cycles. In my work, I am examining the effect of various cell configurations, on natural convection to operate these batteries with minimal external stirring. Our simulation results show improvement in voltage and energy efficiency for some of these designs. Particle Image Velocimetry (PIV) experiments for flow validation, unraveled through COMSOL based simulations is currently being investigated.

Stress relaxation in a bacterial suspension: The active-to-passive transition

Phani Kanth Sanagavarapu, Sankalp Nambiar[1]*, Prabhu Nott, and Ganesh Subramanian*[1]

[1]*Engineering Mechanics Unit, JNCASR, Bangalore*[2]

Suspensions of bacteria such as Escherichia Coli exhibit interesting rheological behavior under Stokes flow conditions. Bacteria can be modeled as slender rods, and unlike rigid spherical particles they induce a rheological response that is strongly dependent on the orientation distribution. Most bacteria swim by executing a run-and-tumble motion and rotary diffusion in the suspension. Under an externally imposed shear flow, their orientation distribution is influenced by all these three factors and shear rate. The relative importance of these factors is governed by two dimensionless numbers, $\gamma\tau$ (Pe, Peclet Number) and τD_r , where τ is the mean duration of a run, D_r is the rotary diffusivity and γ is the imposed flow strength [1]. At low Pe, the shear viscosity of bacterial suspensions is lower than that of the suspending fluid. At high Pe, the shear viscosity is higher than that of the suspending fluid similar to that of suspensions of passive rods [2]. We focus on the transient dynamics of the rheological properties of microorganism suspensions, as they transition from active regime to passive regime. In order to capture the transient dynamics at low Pe, we carry out a perturbation expansion of the orientation distribution (Ω) in terms of Pe around an initial isotropic distribution and solve the governing Fokker-Planck kinetic equation. At very large (infinite) Pe, we obtain Ω from the governing time-dependent advection equation. For the intermediate range of Pe, we solve for Ω numerically by a spectral expansion in the spherical harmonics basis [3]. Once the orientation distribution is obtained, the transient response of the rheological properties is evaluated from the bulk stress.

References:

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Rheology of dense granular chute flow: Simulations to experiments

Sagar Bharatraj, T. G. Murthy[1], and V. Kumaran
[1]Department of Civil Engineering, IIS Bangalore

Granular chute flow, a widely-used system to validate theories has been found to show a marked dependency on the modulations at its base. Simulations reveal a transition between two distinct states, a random disordered state and an ordered state consisting of hexagonally ordered sheets of spherical particles sliding past each other, depending on the base structure. While previous studies examined rough bases made of a random configuration of frozen particles whose size was varied with respect to the following ones, here we consider a periodically modulated base, where a smooth wall at the base is structured as a sine wave of known amplitude and wavelength in the stream-wise and span-wise directions. There exists a critical amplitude, for a given wavelength for the periodically modulated smooth wall base, below which this ordered state is observed. The critical amplitude increases linearly with the wavelength at lower wavelengths, reaches a maximum depending on the system size, and then decreases as the wavelength is further increased. There is flow for angles of inclination from $15° \leq \theta \leq 25°$ for the ordered state and $20° \leq \theta \leq 25°$ for the disordered state. The critical base amplitude is independent of the angle of inclination, and the total flow height. However, the transition is observed only when the spring stiffness for the interaction between particles increases beyond a critical value for both the linear and Hertzian contacts, and no transition is observed for very soft particles. The effect of the spring stiffness on the rheology, validity of the Bagnold scaling, and thus the influence on transition will also be reported. Linear response studies have been carried out by imposing an external perturbation on the ordered state and thus observing the response of the system. These indicate that the system is very unstable to short-wave perturbations with wavelength comparable to the particle diameter.

Initial studies have found similar ordering phenomena in simulations done on flows confined by side walls, if the side walls are smooth. It has been observed that the flow confinement caused by the presence of the sidewalls increases the critical angle of flow initiation. The presence of smooth side walls results in ordering close to the walls, and this affects the flow rheology. The effect of the different types of the sidewalls on the dynamic properties like the flow velocity, stress tensor and structural parameters like the order parameters will also be discussed. Experiments have been conducted on a glass chute, where velocity profiles in the inclined plane flow of glass beads are measured using imaging velocimetry techniques. These reveal a transition in the shape of the velocity profiles as the ratio of the flow depth and the distance between side walls is varied. The angle between the free surface of the flow to the repose angle at low chute angles; the existence of dead zones at the bottom, acting as an erodible base at low angles; the transition of the velocity from that for an erodible bed to the Bagnold flow for a flat frictional bed at a critical angle dependent on the base roughness will also be discussed.

Secondary flows in sheared granular systems

Peter Varun Dsouza *and Prabhu Nott*

Recent work by our group [1] showed the presence of a dilation-driven, secondary flow in a cylindrical Couette system. This flow consists on a single, large vortex that spans the height of the Couette cell. Such a flow may help explain the recent observations of non-local behavior in granular systems [2]. We extend our group's work to other geometries that show such puzzling behavior. We first look at a split-bottom cylindrical Couette cell, which has been studied in many papers in the last decade [3]. We also look at a parallel plate Couette cell with a split bottom where we find the secondary flow to be more complex than a cylindrical Couette cell. We show how this flow persists over different shear rates and fill heights. We show how such a system generates a train of vortices instead of a single vortex.

References:

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Role of hydrogen and oxygen activation over Pt and Pd doped composites for catalytic hydrogen combustion

Satyapaul A. Singh, Karan Vishwanath[1]*, and Giridhar Madras*
[1]*Department of Materials Science and Engineering, University of Toronto, Canada.*

Removal of excess amount of hydrogen in a catalytic route is a safety measure to be implemented in fuel cell technologies as well as in nuclear power plants. Hydrogen and oxygen activation are crucial steps for hydrogen combustion which can be achieved by modifying supports with suitable noble metals. In present study, Pt and Pd substituted Co_3O_4 – ZrO_2 (CZ) were synthesized using PEG – assisted sonochemical synthesis. Effective ionic substitution in CZ supports was analyzed by X-ray photoelectron spectroscopy. Pd and Pt improved H_2 and O_2 activation extensively, which brought down $T_{50\%}$ to 33°C compared with the support. The activation energy of PdCZ catalyst was found to be more than 2 folds smaller (13.4 ± 1.2 kJ mol^{-1}) than CZ. The effect of oxygen vacancies in reaction mechanism is found to be insignificant step with Pt and Pd substituted CZ supports. However, oxygen vacancies play an important role when CZ alone used as catalyst. These results were supported by H_2 – TPD and H_2 – TPR studies on the catalysts. Full conversions were maintained for 50 h of study at 105°C indicating the stability of the catalysts. The hydrogen combustion rate at these conditions is as high as 24.

Supercritical transesterification: an approach towards sustainable bio-diesel production

Neha Lamba, Jayant Modak, and Giridhar Madras

Fatty acid methyl esters (FAMEs) are useful as biodiesel and have environmental benefits compared to conventional diesel. FAMEs are a viable and green alternative to petroleum based diesel. Conventional routes that usually use homogenous acid/alkaline catalysts are fraught with limitation of high production cost because of the pretreatment of feedstock for removal of free fatty acids (FFA) and water and for the purification of the product mixture. Supercritical fluid (fluids, those are above their critical point and having intermediate properties to that of gases and liquids) technologies can be used to synthesize FAMEs at supercritical conditions of methanol, one of the reactants, without the need of adding an external catalyst. These also preclude the use of costly feedstock pretreatment options, which is so centric to catalytic technologies. Interestingly, the solvation of the precursor oils and the reactivity can be modified just by manipulating pressure and temperature. Thus, FAMEs were synthesized non-catalytically from non-edible vegetable oils: neem oil and mahua oil with two different methylating agents: methanol and methyl tert-butyl ether (MTBE). Neem and Mahua oils were chosen as potential candidates as they are non-edible oil and can be indigenously sourced. Apart from methanol, MTBE was also used as an unconventional methylating agent. A batch high pressure reactor was fabricated in-house to conduct and study the kinetics of these reactions. Nearly complete conversions of these oils were obtained within 10 min, by varying the reaction variables such as temperature, pressure and reaction composition. Larger than five times stoichiometric excess of the methylating agent, makes the reaction kinetics nearly independent of its concentration and thus approximately pseudo first order in nature. The rate constants varied in the range of 10^{-3} to 10^{-6} and activation energies were in the range of 60-120 kJ/mol.

WGS activity and detailed kinetic modeling of WGS over platinum based bimetallic ceria

Ravi Kiran Mandapaka and Giridhar Madras

Water gas shift reaction (WGS) is a prominent reaction in reforming applications. The crucial importance of this reaction lies in the abatement of carbon monoxide using H_2O in gaseous form. In recent years, there has been usage of Ceria and noble metal based catalysts for WGS. This includes impregnating and doping ceria with mono metallic like platinum and bi metallic components. This study presents the development of platinum based bi-metallic catalyst and its applicability for water gas shift reaction. The catalyst was characterized by XRD, XPS, TEM, H_2-TPR and BET. The characterization studies revealed that the bi-metallic substitution in ionic state contributing to the significant increase of the OSC of the catalysts which in turn is reflected from the WGS activity.

In this study, a new kinetic model for WGS over bi-metallic ceria catalyst has been proposed. For this, a dual site mechanism has been proposed and the kinetic parameters proposed for the elementary steps are obtained from the literature. Model befitted the experimental data to reasonable accuracy thus portraying the validity of the kinetic parameters.

Ag & Cu impregnated Fe doped ZnO for bacterial inactivation under visible light

Rimzhim Gupta, Jayant Modak, and Giridhar Madras

Interfacial coupling of semiconductor with metal has been demonstrated for inactivation of *E.coli*. Fe doped ZnO was synthesized by sol-gel method that resulted in enhanced absorbance in visible region. Various concentrations of Cu were impregnated on Fe doped ZnO that eventually turned into copper oxide and compared the photocatalytic activity with noble metal (Ag) impregnated on Fe doped ZnO. The obtained materials were characterized by various techniques. The crystal structures were determined by XRD and XPS was used to identify the oxidation states of the elements present in the photocatalyst. The morphologies and microstructures were determined by SEM. The optical absorbance of the photocatalysts was characterized by diffused reflectance spectra. Photocatalytic experiments were conducted for inactivation of *E.coli* using various catalysts. The rate constants obtained for 3 wt. % Cu impregnated Fe doped ZnO was higher than 1 wt. % Ag impregnated Fe doped ZnO. The higher photoactivity of these materials compared to pristine ZnO can be attributed to decreased recombination of the excitons in the synthesized photocatalysts that was validated by photoluminescence. This study indicates the possible employment of copper as a viable substitute for silver for anti-bacterial applications.

New physical insights into shear history dependent polymorphism in PVDF

Amannuel and Giridhar Madras

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer that exists in four crystalline phases (α, β, γ, δ). Among these, the β-phase has received tremendous techno-commercial importance due to higher dipole moment as compared to the other phases and thus many strategies have been explored in the recent past to obtain the β-polymorph of PVDF. In this study, the effect of shear history on crystalline morphology and behavior of PVDF has been investigated systematically by polarized optical microscopy (POM) coupled to a hot stage, Fourier transform infrared spectroscopy (FTIR), differential thermal analysis (DSC), Rheometer and dielectric relaxation spectroscopy (DRS). Thin films of PVDF (120-150 μm) were sheared at different temperatures ranging from 155 to 220 °C and were allowed to isothermally crystallize at 155 °C. When the samples were isothermally crystallized at 155 °C, a remarkable increase in β-phase content was observed. More interestingly, this phenomenon was observed to be shear history dependent. For instance, the samples which were sheared at high temperature (220 °C) reflected in more β fraction as compared to samples which were sheared at lower temperature (155 °C). It is envisaged that the distance between T_{shear} (temperature at which the samples were sheared) and T_{cry} (crystallization temperature) significantly influences the content of β phase in PVDF. This study clearly demonstrates the fact that both shear history and the depth from T_c influences the conformational changes in PVDF.

Using molecular dynamics simulations to understand the role of cholesterol during pore formation in lipid bilayers

Amit Behera, Pradeep S[1], and K. Ganapathy Ayappa
[1]*Center for Biosystems Science and Engineering, IISc Bangalore*

We investigate the interactions of pore forming toxins (PFTs) with cholesterol rich membranes through atomistic molecular dynamics simulations. The PFT of interest is Cytolysin A (ClyA or HlyE). Previous work has shown that ClyA undergoes a drastic conformational change from its water soluble monomeric state to the membrane inserted protomeric state which subsequently oligomerizes to form a pore. Although the role of cholesterol has been widely investigated for a certain class of toxins known as cholesterol dependent cytolysins, the molecular role of cholesterol in alpha-toxins such as ClyA is poorly understood. Recent single molecule experiments show that the conversion rate from the water-soluble monomer to the membrane inserted protomer increases in the presence of cholesterol. Further, lysis experiments in RBCs have a half- life time that were orders of magnitude smaller than that of RBCs when cholesterol is removed. In this work, we attempt to understand the essential but tenuous role of cholesterol using MD simulations. Using 300 ns, all atom MD simulations of a ClyA protomer inserted into a DOPC:Cholesterol (30 %) membrane we illustrate the binding of cholesterol to specific motifs in the membrane inserted N-terminus of the protomer. Using life-time analysis we attempt to locate the presence of specific cholesterol binding motifs on the ClyA protomer. This will shed light on both the affinity of the protomer to the membrane as well as the improved pore forming efficacy in the presence of cholesterol.

Modelling combination therapy of oncolytic viruses with immune checkpoint blockade drugs

Arjun Gopal and Narendra Dixit

The nature of cancer treatments has shifted from immune compromising to immune boosting drugs. Oncolytic viruses and immune checkpoint blockade drugs currently represent the most promising anti-cancer agents. Experiments show that success and failure in combination therapy is dependent on timing the treatments accurately in a sequential manner. This observation is due to the different roles played by interferon which form the keystone of this system by their ability to boost the immune system but also regulate the immune system attack and induce immune escape. A mathematical model was set up to understand the different interactions and find the adequate time gap for tumour control. Our results show that sufficient virus spread is important before boosting the immune system using immunotherapy drugs. The model predicts the time gap for successful treatment of renal tumours in mice with vaccinia virus and anti CTLA-4 checkpoint blockade drugs. The results predict treatment failure if the drug is dosed together with the virus, and success when dosed sequentially. In summary, the model can be used to design better treatment strategies for tumour control in combination therapy.

Antifreeze proteins - a molecular dynamics study

Aswin Vinod and Sudeep Punnathanam

Antifreeze Proteins (AFPs) are expressed in organisms inhabiting cold ecosystems, which help them survive in subzero temperatures. They were first identified by Arthur de Vries and group in late 1960s. Commercially, they find application in many fields, especially in food processing and cold storage. Adsorption-inhibition mechanism is perceived to be the predominant reason for their antifreeze activity of these proteins. AFPs bind on to the surface of ice, leading to a curvature at the surface as the interface grows. The curved interface causes a local depression of the freezing point of ice, because of the Gibbs Thomson effect. The reasons for ice-binding of the protein, however is not very well understood. Molecular Simulations have been employed in the study of AFPs, as they help in a molecular level understanding of the phenomenon. The current study includes molecular dynamics study of a short peptide molecule that has been reported to retard growth rate of ice crystal in simulations and its interaction with surface of ice. The study also looks at the effect of a type-III AFP at the ice-water interface using molecular dynamics. Simulations also have been performed to check for the binding of the protein on the surface of ice. A reduction in growth of the ice has been observed in the presence of the protein.

The lift force and the torque on a disc immersed in a rotating granular material

Bhanjan Debnath, K. Kesava Rao, and Prabhu Nott

Granular materials are widely used in day-to-day life, and granular flow past solid bodies like earth movers, ploughs, inserts, and mixers are common phenomena in nature and industry. Many experiments have been done on the relative motion between the grains and a solid body, resulting in a drag and a lift force on the body. The origin of the drag force has been explained by some researchers, but the physics behind the origin of the lift force is still lacking. Here we discuss the lift force and the torque on a disc immersed in a rotating granular material using the discrete element method. This geometry has not been examined so far except for a preliminary study in our group. Shearing causes the solids fraction to decrease near the disc and the materials below the disc do not dilate as much as the materials above it. The lift force arises because of the higher axial normal stress below the disc than that above it. The axial shear stress on the curved surface of the disc acting in the upward vertical direction also contributes to the lift force.

Development of ionic substituted manganese oxide catalysts for co oxidation

Ch Anil and Giridhar Madras

Manganese oxide (Mn_3O_4) and metal (Cu, Co and Ni) substituted Mn_3O_4 catalysts have been synthesized using single step solution combustion method. Catalysts were characterized using XRD, XPS, SEM and TEM and BET. The particle sizes of the catalysts were between 21 – 27 nm. CO oxidation was carried out over these catalysts. Cu substituted Mn_3O_4 showed the highest activity with full conversion of CO occurring around ~ 225 ^oC. DRIFTS was used to investigate the mechanism of CO oxidation. The reaction was modelled using Langmuir – Hinshelwood mechanism and the activation energy was found to be 44.4 kJ mol^{-1}. The high activity of Cu doped Mn_3O_4 indicates its potential to replace noble metal based catalysts.

Catalytic isomerization in 1-pentene: Density Functional Investigation

Ch. Sai Kumar, Anant D. Kulkarni, K. Ganapathy Ayappa, and Sudeep Punnathanam

Light naptha (C5-C6 hydrocarbon range) isomerization by zeolite acid catalysts is an important process in petroleum refineries to enhance the octane number of gasoline. Over the past few decades, quantum chemical methods are widely employed to study these zeolite catalyzed hydrocarbon reactions on a molecular level. We propose density functional insights on modelling the catalytic isomerization of alkene. The prototype reaction selected for the present study is isomerization of 1-pentene to cis-2-pentene using the cluster model approach. Energetically equally favorable reaction pathway where 1-pentene undergo isomerization to trans-2-pentene has also been explored. We compare the results of three popular density functionals namely B3LYP, PBE0 and M06-2X in conjugation with two different basis sets, namely, a computationally manageable 6- 31G**, and an extensive triple-zeta, def2-TZVP. Thus, we have total 6 model chemistries. The performance of these methods with reference to activation energies, isomerization will be discussed. The present approach was further extended to investigate the reaction with the larger catalyst viz. inside a cage of zeolite-Y. The initial results of large cage calculations are encouraging.

Dry reforming of methane over Ce-pyrochlores

Disha Jain and Giridhar Madras

The objective of the present work was to develop a pyrochlore based catalyst for dry reforming of methane (DRM) that offers high thermal stability and resistance to deactivation. Noble metal (NM: Pt, Ru) substituted $Ce_2M_2O_7$ (M: Zr, Ti) pyrochlores were synthesized by modified Pechini method. The effect of various combinations of metal and support has been studied towards dry reforming of methane and $Ce_2Zr_{1.96}Pt_{0.04}O_{7-\delta}$ exhibited best catalytic activity. The changes in the synthesized samples were studied after the reaction using XPS and TEM to understand the metal-support interaction. *In situ* FTIR studies were performed to study the reaction intermediates formed over the catalyst during the reaction. Based on the spectroscopic studies for $Ce_2Zr_{1.96}Pt_{0.04}O_{7-\delta}$, a dual site mechanism via carbonate and formate formation was proposed for DRM.

Fenton based advanced oxidation processes for water treatment

Gokulakrishnan Subramanian and Giridhar Madras

Wastewater treatment plants that usually employ microbes to degrade organic contaminants cannot degrade "Non-biodegradable" chemicals especially those that are toxic. Consequently, these non-biodegradable contaminants are released in to fresh water bodies leading to the depletion of its quality. Thus, there is increasing demand for an advanced treatment to effectively eliminate recalcitrant pollutants.

Advanced Oxidation Processes (AOPs) are near ambient temperature and pressure water treatment process which involve the generation of hydroxyl radicals in sufficient quantity that could effectively degrade organic pollutants. The most simple and effective way of generating hydroxyl radicals for contaminant degradation is by Fenton process. The Fenton process uses simple iron salts and green oxidant hydrogen peroxide to generate the hydroxyl radical, a strong oxidant (2.7 V) capable of degrading a variety of contaminants. However, the major drawbacks of Fenton processes are slow reduction of Fe(III) to Fe(II) and narrow (acidic) working pH.

In our recent studies [1, 2] we have attempted to address these drawbacks by using low molecular weight redox/photoredox organic ligands.

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Probing the kinetics of protein-lipid interactions in Giant Unilamellar Vesicles (GUVs)

Ilanila.I.P and K. Ganapathy Ayappa

Cell membrane, acts as a semi-permeable barrier protecting the cellular components. Artificial membranes, that can mimic complex cell membranes, can be prepared either as a free-standing membrane (in the form of vesicles) or a supported lipid bilayer membrane (SLB) on a solid substrate. Model membranes typically do not represent the crowded environment encountered in real membranes and do not account for the presence of an active cytoskeletal network. The main objective of this work is to systematically develop crowded membrane vesicle platforms and study the interaction of pore forming toxins, synthetic polymers and nanoparticles with these membrane platforms by understanding the change in dynamics of vesicles. Preliminary studies were carried out with Giant Unilamellar Vesicles (GUVs) as a model system to understand kinetics of pore formation and the change in lipid dynamics due to the interaction of the pore forming toxin, Listeriolysin O, with the bilayer membrane. Listeriolysin O, a cholesterol dependent cytolysin, has been reported to oligomerize to form pores in the cell membrane and cause cell lysis. In our experiments, we observed GUV membrane fluctuations during the oligomerisation process and the time taken for the contents of GUV to leak out through these pores was found by intensity measurement. The experiments also indicated that the kinetics of pore formation depends on the lipid composition of the membrane. Though the dynamics of lipids during oligomerisation is yet to be studied, the toxin is found to reduce the diffusivity of the lipids in the membrane after 30 min of incubation.

Suction Microfluidics: Architecture and Applications

Jatin Panwar, Priyanka V, Suraj Jagtap, and Rahul Roy

Droplet Microfluidics has proved its potential as a major tool in scientific explorations at microscale, but the facilities and resources required for its fabrication and operation still pose a challenge on their economic viability and mobility, hindering the extension of their applications as point of care and diagnostic or biochemical sensing and analysis devices in areas ranging from a remote underdeveloped village to international space station and beyond.

The traditional microfluidics depends upon a flow rate controlled approach to push the fluids into the system, which requires multiple syringe pumps and sophisticated flow stabilizers. We propose an alternate mechanism of pressure difference driven droplet generation using suction, replacing multiple syringe pumps with just a syringe used as vacuum source. This improves the compatibility, mobility and operation cost significantly, especially when the device has multiple unit operations with multiple fluid inputs. The flow rate distribution among the carrier and dispersed phase fluids is controlled by the geometry of microfluidic channels overcoming the need of any external flow stabilizer. We provide a quantitative analysis of design parameters that governs the droplet dimensions and dynamics inside a flow focusing channel. We also demonstrate our method by employing it in a microfluidic device used to amplify and quantify nucleic acids in single cells.

Study of high Mach number turbulent flow in a channel by DSMC simulations

R. Mani Sravani and V. Kumaran

The transition and turbulence in the flow of a gas through a channel is the subject of the present study. The flow of gases at high velocities is characterized by two dimensionless numbers, the Reynolds number which is the ratio of inertial and viscous effects and the Mach number which is the ratio of the gas velocity and the speed of sound. While turbulence and the laminar- turbulence transition for low Mach number incompressible flows has been extensively studied, there is relatively little work on transition and turbulence at high Mach numbers. Here, the modes of transition to turbulence in a channel are studied at high Mach number. It is shown that when the Mach number exceeds a critical value, the transition takes place through a mechanism that is different from that in incompressible flows. The mode structure for the most unstable modes are identified. The flow after transition is studied using the Direct Simulation Monte Carlo (DSMC) method. DSMC is a very simple and versatile method used to simulate near-continuum flows on a rarefied or hypersonic gas at individual molecular level. It is known for its computational efficiency and ability to model details at molecular scale. The main interest of the present work is to characterize turbulence of a rarefied gas through a channel in compressible limit (Ma greater than 0.3) by DSMC simulations. Validation with previous results for low Reynolds number was done, followed by simulations at higher Reynolds number. Linear Stability Analysis was also done in both incompressible and compressible limits to get critical Reynolds number.

Study of the mechanical behaviour of hair fiber

Naveen Kumar and Prabhu Nott

Human hair fiber is very complex biological material. It is a keratinous fiber consisting of intermediate filaments embedded in the amorphous matrix. The intermediate filaments are responsible for the crystalline part of the hair fiber. The stress-strain curve of hair consists of three regions, pre-yield, yield and post-yield region at different strain levels. These regions are correlated with the transformation of the physical bonds present in the hair structure. The phenomenological rheological models are used to study the mechanical behavior of hair fiber. Stress relaxation experiments are done to study the mechanical behavior of hair fiber. Dry hair is modelled with the help of 5-parameter generalized Maxwell model, while wet hair is modelled using 3- parameter Maxwell model. The different relaxation times are represented by the Maxwell arms in the model and are related to the relaxation of actual physical bonds present in the hair structure.

Towards DNA origami-based magnetic nanopropellers

Nuruddin Bahar[1], Abhijith Raghuprasad[1], Ambarish Ghosh[1], and Banani Chakraborty
[1]Centre for Nano Science and Engineering (CeNSE), IISc Bangalore

Through DNA nanotechnology one can design very complex nanostructures via a bottom-up fabrication method. These nanostructures are now embarking in the field of application. To test the application of six-helical bundle DNA origami we wish to mimic a silicon di-oxide-based nanopropeller, which is demonstrated using top-down nanotechnology [1]. A two-fold approach is adopted in this respect. First is to modify the silicon dioxide nanopropeller (SiO_2-NP) with magnetic nanoparticle to observe their movement under magnetic field *in vitro* first. Second is to build the nanopropeller using DNA origami through bottom-up nanotechnology where we can modify the nano-helix bundles with iron-oxide magnetic nanoparticles to be studied under a magnetic field [2]. A couple of variants of these magnetic helices will be made for checking the movement with fluorescence microscopy and atomic force microscopy. Here, we describe a simple method for folding long, single-stranded circular genomic DNA from M13mp18 phage as the scaffold strand into cylindrical shaped 6-helix bundles (6HB) [3] as shown in figure 1.

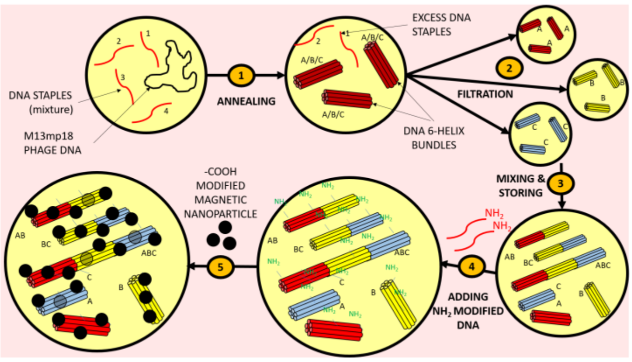

Figure 1: Experimental flow to make magnetic nanoparticle modified DNA origami nanopropeller

Magnetic iron oxide nanoparticles (10-20nm) are programmed to connect to 6HB at a distance of 30 nm along the backbone of 6HB through a covalent coupling of 5′ end of NH_2-modified DNA with COOH-modified magnetic nanoparticle. Aim is to generate a biocompatible propeller system, which can mimic an artificial flagellar assembly similar to an *E.coli*. Using sticky-ended cohesion, we are able to control the precise length of these 6HB to grow in multiples of 400 nm to more than 1 µm in length. Currently we are characterizing the formation of these assemblies and nanoparticles in parallel to put them together and study their behavior further.

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Water adsorption on graphene oxide

Rajasekaran M and K. Ganapathy Ayappa

Graphene oxides are graphene sheets with surface and edge carbon atoms having functional groups. The functional groups consist of epoxy, hydroxyl and carboxyl groups. As a consequence, graphene oxides have hydrophilic and hydrophobic regions at the molecular level. Recently, it has been found that graphene oxide is a promising material for water desalination. Graphene oxide membranes have been found to exhibit higher water flux (4 - 10 times higher than current nanofiltration membranes). The GO membranes have also shown higher selectivity towards CO_2 even in humid conditions. The graphene oxide membranes show higher selectivity for hydrogen in H_2/CO_2 and H_2/N_2 mixtures. Hence they are promising materials for gas separations. Other applications of graphene oxides include printable electronics, solar cells, fuel cells and bio-sensors. In order to understand the high permeabilities reported for graphene oxide membranes in aqueous solutions, it is important to study the molecular interactions of water at the graphene oxide interface. Our study focuses on the adsorption of water on graphene oxides using grand canonical Monte Carlo simulations. We have carried out plane wave periodic density functional theory calculations to optimize the molecular structure of graphene oxide. The partial atomic charges are derived using ab-initio Hartree – Fock method and the atomic charges are obtained using CHELP-G scheme. These charges are used in classical Monte Carlo simulations. The optimized potential for liquid simulation (OPLS-AA) forcefield is employed in classical Monte Carlo simulations.

GCMC simulations reveal interesting water film growth as the vapor pressure is increased. Water is found to initially adsorb at the hydrophilic - hydrophobic interface. Subsequently water bridge spanning the hydrophilic region is observed. Hydrophobic/Hydrophilic ratio plays a key role in water layering and organization on the GO surface and adsorption isotherms. Separated water islands with increasing hydrophobicity is observed. Large number fluctuations are observed in graphene oxide due to the Janus nature of the interface.

Step towards mimicking biology with DNA origami-graphene hybrid nanopore

Ramkumar B[1], Sohini Pal[1], Banani Chakraborty, Prabal K Maiti[2], Akshay Naik[1], and Manoj Varma
[1]Centre for Nano Science and Engineering (CeNSE), IISc Bangalore
[2]Department of Physics, IISc Bangalore

Biological nanopores are formed by pore-forming proteins, typically a hollow core passing through a mushroom-shaped protein molecule. Examples of pore-forming proteins are alpha hemolysin and MspA porin. These are great for sensitivity but the proteins are difficult to handle. To mimic this biological nanopore we have taken help from top-down and bottom-up nanotechnology to fabricate a bilayer nanopore. Scaffolded DNA origami [1] is also a novel and unique method to fabricate tailor- made nanostructures with wide range of applications. The major advantage of DNA origami is the accurate control over the shape of the structure at the nanometer level. Combining DNA origami on the top layer with solid-state nanopore on the bottom layer we aim to introduce great many possibilities for changing and enhancing pore properties and features. In our design, we are using a DNA origami Nanopore (Bottom-up nanotechnology) structure to modify a Graphene Nanopore (Top-down nanotechnology). [2] The specific interactions between programmed nanopores of DNA origami and the translocating DNA strand might cause different residence times and ionic currents, based on various guest interactions. The graphene on the other hand with its atomically thin layer will be helpful in measuring the blockage currents due to single molecules. We have started with designing two Rectangular origamis with pores 5nm/5nm and 2nm/2nm at their centres respectively using caDNAno software.[3] We are modifying the selectivity of the pores using different lengths of overhangs which are single stranded DNA interacting with translocating DNA in this case. The relation between pore design, number of overhangs and the corresponding effects in translocating time are also being analysed using all atom fine grain Molecular Dynamics (MD) simulations. This hybrid nanopore will be helpful in single molecule detection and can have other biomolecule sensing applications too.

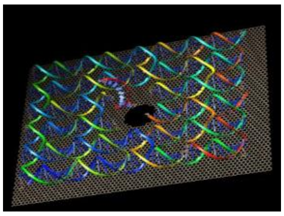

Figure 1: Overview of the hybrid nanopore system

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Using mathematical models to improve the treatment of hepatitis C virus (HCV) infection

Rubesh Raja, Vishnu Venugopal, Pranesh Padmanabhan, Aditya Pareek, Kapil Newar, and Narendra Dixit

HCV affects hepatocytes (liver cells) causing chronic infection. Currently, 185 million people in the world are chronically infected with HCV. Direct-acting antivirals (DAAs), drugs targeting specific viral proteins, are used in HCV treatment. These drugs are genome-specific, and HCV escapes them by mutating itself. The pre-existence of HCV genomes carrying mutations resistant to DAAs can compromise treatment outcomes. We developed a multiscale mathematical model of HCV within-host viral dynamics and evolution to predict frequencies of drug-resistant mutants that may exist below current detection limits. Interferon-α (IFN), an immune modulator which triggers a generic antiviral immune response, is also used in HCV treatment in combination with DAA. These drugs are not genome-specific, but still, HCV escapes them by making the hepatocyte refractory to IFN. HCV induces bistability in the IFN signalling network creating a stable state where HCV can persist. Here using a multiscale description of intracellular IFN-HCV bi-stable system and extracellular within-host viral dynamics, and the population-level distribution of IFN-refractoriness we predicted the treatment outcome of IFN treatment.

Next, we observed that patients who failed DAAs treatment have greater IFN-refractoriness, a surprising correlation given that DAAs target specific viral proteins whereas IFN triggers a generic antiviral immune response. We constructed a mathematical model that integrated cellular responses to IFN, within-host viral dynamics and evolution, and the population-level distribution of IFN-refractoriness, and therefore had the power to evaluate causal links between IFN-refractoriness and the response to DAAs. Model quantitatively captured response rates observed across clinical trials involving DAAs, elucidated the origins of the failure of DAAs, and predicted that a personalized increase of DAA dosage and/or addition of IFN could avert treatment failure.

Characterizing DNA aptamer based biosensors using single molecule spectroscopy and fluorescence lifetime imaging microscopy

Saurabh Umrao, Anusha Murthy, Banani Chakraborty, Rahul Roy, Julien Reboud[1], and Jonathan Cooper[1]
[1]Biomedical Engineering Research Division, School of Engineering, University of Glasgow, United Kingdom

Every day, the need to detect biologically relevant molecules such as small molecules, proteins, cancer markers, etc is increasing. However, converting the biological information to electronic/optical signal is sometimes challenging due to complex biological environment in vivo. This challenge has led the researchers around the globe to develop of biosensors, which employ biomolecules to recognize the cellular target and utilize output elements to translate the biorecognition event into electrical, optical or mass-sensitive signals. One such strategy employs DNA Aptamers. Aptamers are single stranded/double stranded DNA molecule that bind their target with high specificity. Our current work focuses on an adenosine binding DNA aptamer (ABA) that undergoes considerable conformational changes upon cooperative binding of two adenosine (or ATP) with dissociation constant (Kd) below 10µM. The aptamer structure is known to fold and create two pockets for adenosine binding. However detailed understanding of conformational kinetics and cooperativity of aptamer target binding is lacking. Single molecule methods like smFRET not only allow us to measure the conformational changes induced by the ligand binding, but also allows real-time tracking of the structural changes in individual molecules. Using Adenosine binding aptamer (ABA) as model DNA aptamer, we report real-time aptamer structural transitions upon ligand binding and how adenosine stabilizes the folded state. We have further used ABA to build a new platform for wash less detection of adenosine using fluorescent lifetime measurements that can bypass limitations of current immunoassays. It has been demonstrated that conformation change in DNA aptamers can lead to change in fluorescence lifetime of specific dyes conjugated to aptamers, which has been used for heterogeneous immunoassays. However direct assays, where the analyte is detected without the need for a subsequent labeling step after capture, are highly advantageous as they are easier to implement ('one pot assays') and less prone to non-specific signals due to the reporter chemistries (e.g. secondary antibodies). Here, we report the development of a fluorescence lifetime based homogeneous (or 'wash-free') assay, using ABA to detect adenosine directly from blood samples. This shows the potential of lifetime measurements on aptamers as a biosensor, a platform which can be adapted to a large number of target molecules through the versatility of aptamer design and selection.

Synergy between innate and adaptive immune responses may decide the fate of HCV infection

Subhasish Baral, Rahul Roy, and Narendra Dixit

Hepatitis C virus (HCV) infection can either get cleared spontaneously (in 20-40% cases) or cause persistent infection leading to liver cirrhosis and hepatocellular carcinoma. Why some infected individuals clear the infection spontaneously and others do not is still unknown. Humans have two arms of the immune response, the innate immune response, which gets triggered early during infection, and the adaptive immune response, which gets induced after a few days to weeks. CD8$^+$ T cells are part of the adaptive immune response and are essential for clearance of the pathogen. However, experiments show that the innate immune response was stronger in hosts that cleared the infection compared to hosts that got persistently infected. Here, by modelling we show a synergistic effect between innate and CD8$^+$ T cell responses. We find that though the innate immune response cannot clear the infection alone, variations in its strength can impact CD8$^+$ T cell dynamics leading to drastic differences in final outcomes. The observed synergy explains the observation of early treatment with interferon-α leading to higher sustained virological response (SVR) rates compared to late initiation of treatment. We also show that the origin of synergy is a dynamical motif, which not only plays a pivotal role in HCV infection but is also present in other settings like cancer and other viral infections such as lymphocytic choriomeningitis virus (LCMV) in mice and human immunodeficiency virus (HIV) infection of humans.

Insights of preferential CO oxidation mechanism over copper substituted cobalt oxide supports

Suhas Mukherjee, Satyapaul A. Singh, and Giridhar Madras

Achieving higher conversion and selectivity towards CO oxidation under H_2 rich conditions (called as preferential CO oxidation (PrOX)) is still a challenging task at low temperatures. The versatile applications such as three way catalytic converters equipped with IC engine and for proton exchange membrane fuel cell (PEMFC) requires the low temperature CO removal for enhancing the economy of the process. High purity hydrogen gas with less than 10 ppm of CO is required for PEMFC operation because of its anode poisoning effects due to CO. The noble metal catalysts (Pt, Pd, Rh, Au and Ru) are found to be attractive for these applications due to their strong interaction with carbon monoxide molecules. However, the low-cost materials for PrOX catalysis are quite unexplored.

In present work, an attempt has been made to understand the mechanism of PrOX reaction with low cost materials such as cobalt oxide with copper substitution. Cobalt oxide (Co_3O_4) supports and Cu substituted cobalt oxide were prepared using sonochemical synthesis. Temperature sensitivity on CO oxidation reaction was studied with the different loadings (0 – 5 at%) of dopant to understand the optimized composition of Cu. Temperature corresponding to maximum conversion of CO to CO_2 was found to be 110°C when the reaction was carried out with 3 at% Cu/Co_3O_4 ($Cu_{0.09}Co_{2.91}O_4$) at gas hourly space velocity (GHSV) of 47800 h^{-1}. Activation energies of these catalysts were found in the range of 24-36 kJ mol^{-1}. $Cu_{0.09}Co_{2.91}O_4$ exhibited maximum apparent rate of reaction for CO oxidation. Among all the prepared catalyst of $Cu_{0.09}Co_{2.91}O_4$ was found to be the most active catalyst for PrOX reaction as well. In order to find Cu substitution in the Co_3O_4 each of the catalysts were characterized using X-ray diffraction technique. Prepared catalysts exhibit promising selectivity towards CO oxidation reaction compared to precious materials reported in literature. *Insitu* Fourier transform infrared spectroscopy (DRIFTS) study has been carried out in order to understand the behavior of reaction intermediate species and possible reason for superior performance of the catalysts. In this study, the formation of active carbonate species even at temperatures as low as 50°C on $Cu_{0.09}Co_{2.91}O_4$ has been noticed under PrOX conditions. The possible reason for higher catalytic activity of $Cu_{0.09}Co_{2.91}O_4$ could be attributed to formation of active intermediate species during the reaction.

Self-assembly of M13 bacteriophage

Suraj Jagtap, Anayat Bhat, Jatin Panwar, and Rahul Roy

Filamentous bacteriophage has wide applications in areas, such as DNA nanotechnology, antimicrobial treatments, gene therapy, and electronics because of its easier and less cost of production. We select M13 as a representative filamentous bacteriophage. M13 phage has high aspect ratio of 100-160, with the length of 800-1000 nm and diameter of 6-8 nm. It infects and replicates inside the Escherichia coli (E. coli) carrying F-pilus. Newly formed particles assemble on the membrane and eject out of the cell without lysing it. Assembly process of phage has not been studied well so far. Previous studies of the M13 assembly process were based on the bulk phage production from the bacterial cells in bulk. Usually, there is a large heterogeneity in cellular response, which plays a role in deciding the average behaviour. Hence we use single molecule and single phage fluorescence microscopy to study the assembly at the single cell level. The images are taken after labeling M13 with specific antibodies. The size of M13 is beyond the resolution of the microscope. Hence super-resolution imaging technique is applied to capture the images of the assembly process. The images show the localization of the assembled sites near the polar and septum region of the bacteria.

To study the kinetics of the assembly process, mobility of one end of the virus coming out of the host cell is used. The movement of the labeled antibody attached to the phage is captured. The diffusion coefficient of this antibody can be correlated to the length of a phage hanging out of the cell membrane, which can provide the rate of phage coming out of the host cell. Also phage production rate can be found out by trapping a single infected cell inside the droplet and counting the viruses produced as time progresses.

In future, we will try to find out the minimal components required for the assembly to carry out the assembly process in vitro. Lipid vesicles can be used to replicate the cell membrane of the bacteria.