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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**

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 protecting underlying tissue from infection, dehydration, chemicals and mechanical stress. While corneocytes of SC remain almost impermeable, 95

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

**S. Bhattacharya**

IS

Indian Institute of Technology 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**

- [1] W. Lu et al., Biol. Chem. 394, 15-27 (2013)
- [2] M. Mukherjee, M. Vajpai and R. Sankararamakrishnan, BMC Genomics 18, Art. No. 560 (2017)
- [3] M. Mukherjee, A. Gupta and R. Sankararamakrishnan, Biophys. J. (2020) In press.

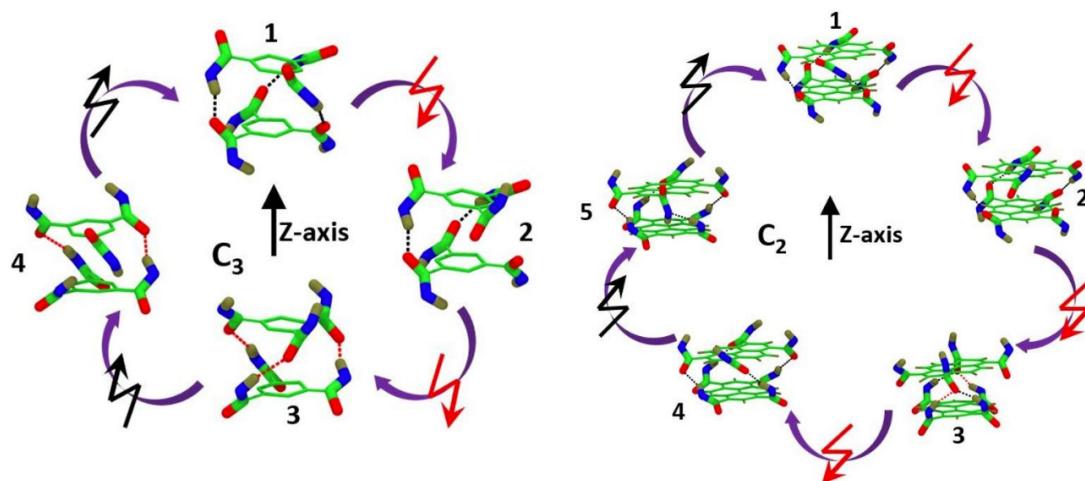
# Modelling Supramolecular Polymers

B. Sundaram

KL

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

- [1] Zhou, H.-X.; Rivas, G. ; Minton, A.P. *Annu. Rev. Biophys.* 2008, 37, 375-397.
- [2] Wang, K.-H.; Chang, C.-W. *Phys. Chem. Chem. Phys.* 2015, 17, 23140–23146
- [3] Sukenik, S.; Politi, R.; Ziserman, L.; Danino, D.; Friedler, A.; Harries, D. *PloS ONE*, 2011, 6, e15608.

# **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>**

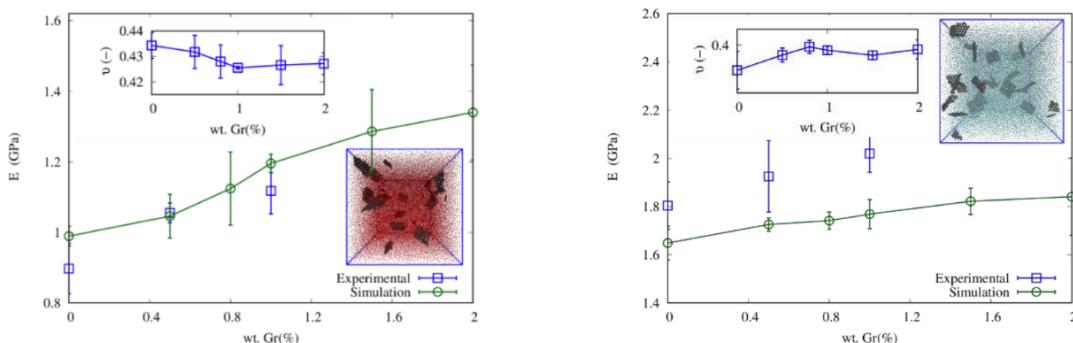
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Graphene, being one of the most promising material, has gained attention in scientific and industrial fields. With its superior properties, if introduced in the polymeric matrix can potentially improve material characteristics (such as thermal, elastic, 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

- [1] E. Panizon, et al., J. Phys. Chem. B, 119 (2015), 8209-8216.
- [2] X. Li, et al., Acta Mechanica Solida Sinica, 30 (2017), 557-682.
- [3] F. Müller-Plathe, J Chem Phys, 106 (1997), 6082.
- [4] R. Guo, et al., Polymers, 11 (2019), 549-568.

## 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

**S. Maheshwari<sup>1</sup>, C. v. Kruijsdijk<sup>2</sup>, S. Sanyal<sup>1</sup>, A. Harvey<sup>3</sup>**

IS

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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

**U. Saxena, S. Chouksey, K. Rane**

IS

Indian Institute of Technology, Gandhinagar, India

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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IS

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

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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**

**P. K. Jha**

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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**

**A. Das<sup>1,3</sup>, P. Sahu<sup>2,3</sup>, Sk. M. Ali<sup>2,3</sup>**

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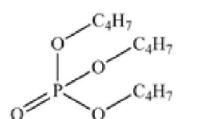
# Study of Water Extraction by Phosphate Ligands by Experiments and Molecular Simulations

D. U. Bapat, V. H. Dalvi

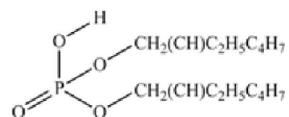
IS

Department of Chemical Engineering, Institute of Chemical Technology, Mumbai

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].

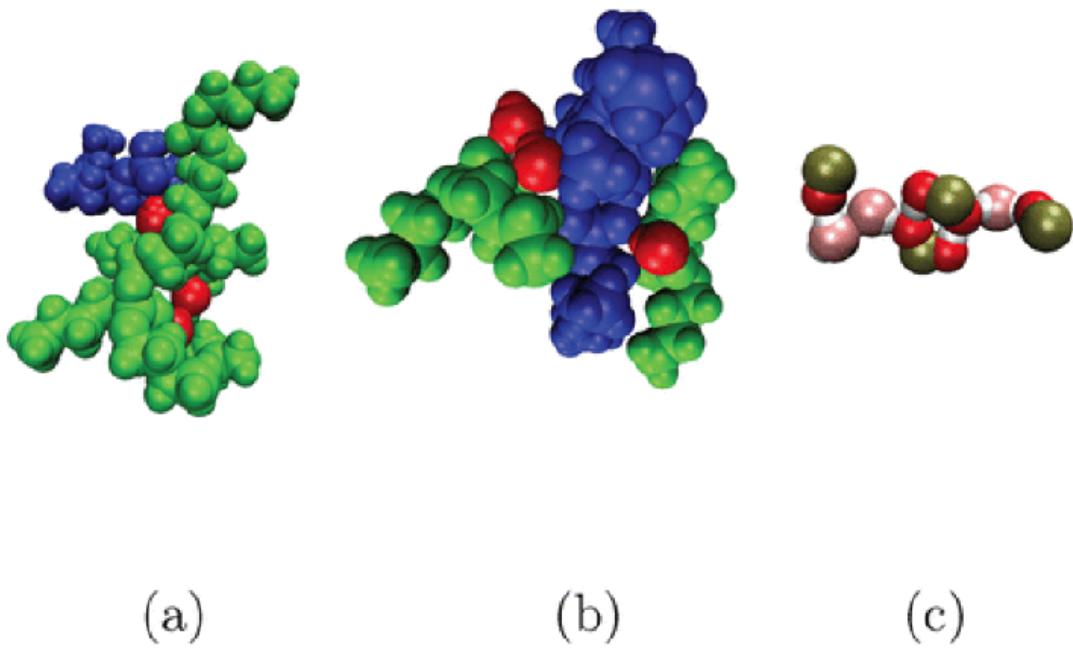


Tributylphosphate (TBP)



Bis(2-ethylhexyl) hydrogen phosphate  
(D2EHPA)

**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**

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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  $T_m = 319.6 \pm 2.3$  K for DPPC bilayers, within a few Kelvin of the experimentally observed  $T_m = 314.5$  K, while the previous best estimate of  $T_m$  via conventional simulated melting with the same force-field is  $\approx 334$  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

## Tuesday Session

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

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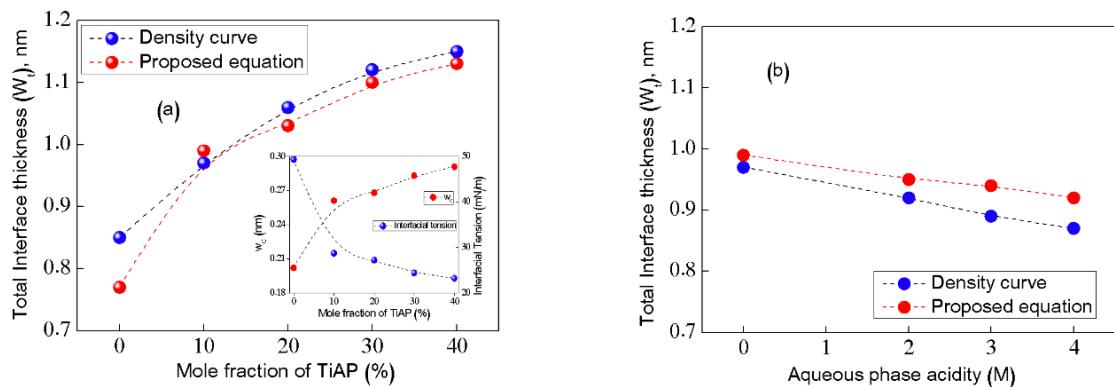
Microscopic understanding of the interface between two immiscible or partially miscible liquids for a biphasic system not only has an immense interest in view of mass transfer processes but also has significant technological importance in the field of science and engineering. Due to its inherent difficulty, 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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