A Message from the PIRE Project at City College of New York

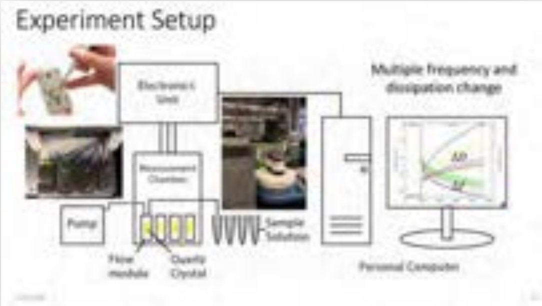
Masahiro Kawaji
Professor and Director of the PIRE Project

I am pleased to issue our second PIRE Newsletter after a long delay due mainly to the COVID-19 pandemic which has caused lab shutdowns at CCNY and other collaborating institutions in Europe. Following a site visit by the US National Science Foundation in September 2019, research activities and collaborations were intensified leading to a total of eight new publications (published and accepted). However, the pandemic forced us to cancel PhD and undergraduate student internships at collaborating institutions in Norway and France, and also caused the postponement of the Third Annual Review Meeting until late January 2021. Since the start of this project in October 2017, three PhD students and five Master's students have completed their programs and graduated, with two more PhD students nearing graduation as well. Two new PhD students and one Master's student have recently joined our project to continue the collaborative research efforts. In the past year, four speakers were invited to give lectures on topics of interest to PIRE, and six Research Thrust meetings have been held remotely. Project Integration meetings have also been held three times to enhance our understanding of common issues among all Research Thrusts, such as wetting phenomena at interfaces, and to learn advanced measurement techniques involving X-ray, Gamma-ray and NMR.

Second Annual Review Meeting Postponed

The project's Second Annual Review Meeting was scheduled for June 2020 in Paris. Unfortunately, due to the COVID-19 pandemic, the meeting was cancelled. We are working with our collaborators to hold a virtual meeting in late January. And if all goes well, we hope to safely gather in Paris in the summer of 2021.

Research Thrust Meetings

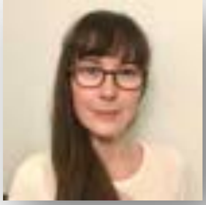


Thrust meetings are held to enable PIRE Project faculty and students to interact and collaborate with international researchers. These meetings include presentations by the thrust Ph.D. and undergraduate students from CCNY, European collaborators and industry professionals. Each presentation is followed by a series of questions and comments, with additional time provided for general discussion at the end of each thrust meeting. All of the thrust meetings are open to participation by members not only of that particular thrust, but of all existing PIRE Project Research Thrusts.

Project Integration Meetings

The PIRE project holds regular project integrations meetings. The purpose of these meetings is to identify and discuss common issues of interest to all the Research Thrusts in PIRE, such as wetting and interfacial properties. All the PIRE faculty and most of Ph.D. students attended this meeting to observe actual fluid samples investigated in various Thrusts. The first meeting was focused on the wetting phenomena which play a significant role in the formation and behavior of gas hydrates and other complex fluids.

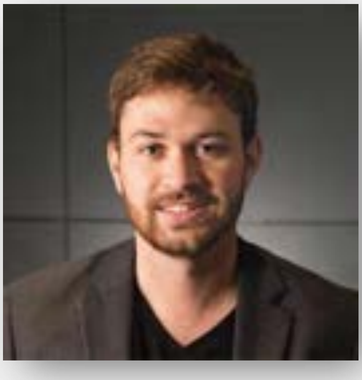
Welcome to our Project Coordinator



Sumer Mishue joined the PIRE project in October of 2019.

MRI and Computational Modeling of Multiphase Flow Systems

October 15, 2019



Professor Chris Boyce
Columbia University

Multiphase granular flows are encountered ubiquitously in nature as well as energy, chemicals and pharmaceuticals industries. Despite their importance, these flows are poorly understood in part due to a lack of robust experimental techniques for detailed characterization of the fluid and particle motion in 3D systems. Here, we present the capabilities of multichannel magnetic resonance imaging (MRI) to image particle concentration and velocity fields non-invasively in 3D granular flows with millisecond resolution. We use these capabilities to image previously unseen flow phenomena in fluidized beds and quantify the effects of changing parameters such as gas flow rate, particle size and amount of liquid injected on bed hydrodynamics. We demonstrate the ability for MRI to measure gas, liquid and particle flows separately in multiphase granular flow systems to test assumptions in computational and empirical models. We also use computational modeling to identify the mechanisms underlying anomalous flow phenomena. Further, we demonstrate the ability of vibration combined with gas flow to create controllable structured flows in granular materials and investigate bubble behavior in dense suspensions.

R&D in Multiphase Flows in the NUEM-UTFPR

November 21, 2019

Professor Rigoberto Morales
University of Parana, Brazil

The Multiphase Flow Group (NUEM) of the Technological Federal University of Paraná (UTFPR) has over 10 years of experience in the development of both applied and fundamentals research on multiphase flows in pipes and equipment. The NUEM is located on a 3,200 m2 and has the following labs: Multiphase Flow, Flow Assurance, Instrumentation, Flow Visualization, and Computational Fluid Dynamics. Several research projects sponsored by major oil and gas companies and governmental funding agencies have been developed at NUEM. Presently, NUEM has over 60 people amongst professors, researchers, technologists and undergrad and graduate students. In this seminar, details of the research activities developed at NUEM will be presented. Emphasis will be given to the following subjects currently under development: modelling and experimental multiphase flows in pipes with hydrate formation, 3-phase oil-gas-water separation systems and sensors for phase detection in multiphase flows.

Fluid/fluid interface engineering and its energy applications

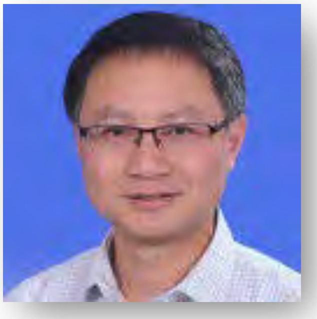
February 10, 2020

Professor Siyoung Choi
Korea Advanced Institute of Science and Technology

How fluid/fluid interfaces can be engineered for two energy applications, polymer electrolyte membrane fuel cell (PEMFC) and redox flow battery (RFB). The first part of the talk includes a PEMFC catalytic layer that requires fast transport of reactants (proton and oxygen) and fast drainage of a product (water). To satisfy all the requirements, which is extremely difficult to achieve by conventional methods, we fabricate a macroporous PEMFC catalytic layer using a high internal phase Pickering emulsion template. Pt/C particles used as an emulsion stabilizer are exposed to the catalytic layer surface to maximize the reaction of proton and oxygen while interconnected macroporous network of ionomers supports the entire catalytic layer. The second part is about a membrane of the vanadium RFB system. It generally requires high proton conductivity and selectivity over vanadium ions. We use the conventional ionomer membranes (Nafion) that have high chemical/mechanical stability, but is expensive. By controlling their internal nanostructures using fluid/fluid interfaces, we could decrease permeability of vanadium ions by 1000 folds, thus reducing the membrane thickness as low as tens of nanometers while keeping the similar proton conductivity.

Unlocking the Value of Petroleum Through Structure Characterization with Molecular Imaging

December 3, 2020



Dr. Yunlong Zhang
ExxonMobil
Research & Engineering

The energy industry is facing a grand dual challenge today, created by the need to reduce carbon emissions for the environmental sustainability, while keeping up with the world demand for the energy and materials. Fundamental research is instrumental to address these challenges by developing new technologies and providing new opportunities. In this talk, I will present the research on an emerging frontier by applying the molecular imaging technique to petroleum, and some recent progress in understanding petroleum structures, reactivities and properties.

Characterizing the chemical structure of petroleum is a formidable scientific challenge due to the great diversity of molecules in the complex mixture. Despite tremendous previous effort dedicated to structure characterization using various advanced techniques, the definitive determination for the chemical structures of individual heavy petroleum molecules has eluded us. Non-contact atomic force microscopy (nc-AFM) now provides this capability. A number of challenges need to be addressed to achieve its full potential. For example, sample molecules need to be desorbed with the flash heating method to deposit onto the substrate surface for imaging; hence, the sample integrity during this process is uncertain. In addition, the representativeness of imaged molecules from a molecular mixture is unknown. Further, the interpretation of AFM images relies heavily on people's knowledge and experiences, and it is especially challenging for nonplanar structures such as those in petroleum asphaltenes. Many of these challenges have been addressed recently by studying various model compounds. These results have proved to be valuable in studying real petroleum mixtures and addressing various questions on the structure of petroleum asphaltenes. Novel structural features have been discovered and important new insights into the reactivities of petroleum hydrocarbons have been obtained. Importantly, new reaction pathways have been identified, which paved the road for alternative uses of petroleum molecules for making carbon materials. Therefore, the value of petroleum molecules can be unlocked by knowing their molecular structures.

Thrust 4
PCM Nanoemulsions
December 17, 2020

Masahiro Kawaji
Thrust Leader

- Jungeun Park " Molecular-Level Understanding of Phase Stability in Octadecane-Water-Stearic Acid Phase-Change Nano-Emulsion for Thermal Energy Storage "
- Artur Zych "Thermal Stability of Nanoemulsion PCM by Span 60 and Tween 60"
- General discussion – Future research collaboration

Thrust 3
Drilling Fluids
November 30, 2020

Sanjoy Banerjee
Thrust Leader

- Titus Ofei: "Barite sag measurements at HPHT conditions/Temperature dependence of viscosity models"
- Dinesh Kalaga and Andres Velez Mendoza: "Particle settling velocity in Taylor - Couette cells and synthesis of stable water-in-oil emulsion"
- Blandine Feneuil: "Sedimentation and creaming of emulsions containing particles"
- General discussion – Future research collaboration

Thrust 2
Gas Hydrates
October 29, 2020

Jeff Morris
Thrust Leader

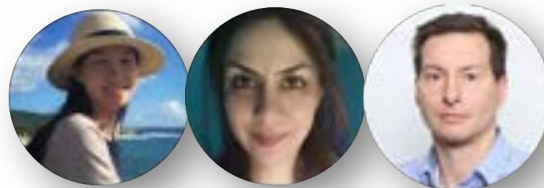
- Raj Ramamoorthy, LGC: DSC coupled optical microscopy experiments
- Nicolas Cinq, LCPQ: Preliminary results from CO_2 and cyclopentane hydrates simulations
- Didier Dalmazzone, ENSTA Paris: Measurements of thermodynamic properties of CP + CO_2 mixed hydrates
- Jeff Morris, CCNY: Update on current work under COVID

PIRE at the City College of New York — Thrust Meetings

Thrust 1
Asphaltenes
January 27, 2020

Robert Messinger
Thrust Leader

- Fang Liu, CCNY - “Mixture Effects in Asphaltene Absorption at Liquid-Liquid Interfaces”, and “Study of Asphaltene
- Deposition on Solid Surfaces”
- Shaghayegh Darjani, CCNY “Molecular dynamics study of adsorption of asphaltenes at Oil/water interface”
- Martin Fossen, SINTEF, "Plans for Shaghayegh Darjani’s Asphaltene Research in Norway – Direct Fractionation of
- Asphaltenes and Subsequent Characterization"



Thrust 2
Gas Hydrates
January 24, 2020

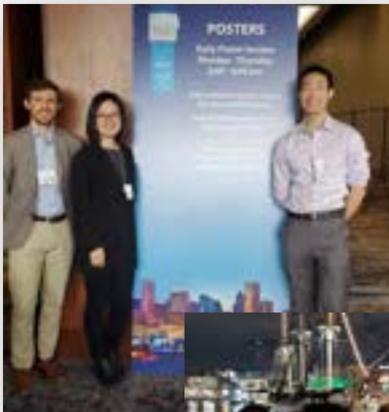
Jeff Morris
Thrust Leader

- Jeff Morris, CCNY: 2020 planning - Initiation of a Thrust objective: Process/Flow Assurance Synergy
- Didier Dalmazzone, ENSTA Paris: "MUSCOFI update and an introduction"
- Martin Fossen, SINTEF: "Update & some recent results"
- Sebastien Teychéné / Raj Ramamoorthy, LGC: 2020 Plans - "crystallization experiments"
- General discussion - Aude Simon – varied issues, e.g., type of hydrates best for study by the DFTB method

Thrust 3
Drilling Fluids
November 25, 2019

Sanjoy Banerjee
Thrust Leader

- Masahiro Kawaji, CCNY: “Summary of NSF Site Visit”
- Bjornar Lund, SINTEF: “Research and publication plans"
- Titus Ofei, NTNU: “Influence of static and dynamic conditions on Barite sag and stability in OBM: experimental results"
- Blandine Feneuil, University of Oslo: “Study of sedimentation of particles in emulsions"
- Dinesh Kalaga, CCNY: “Sedimentation of weighting material and drilling fluid’s rheology”



PIRE-sponsored CCNY chemical engineering student Jay Park gave a poster presentation, "Molecular-Level Understanding of Phase Stability in Octadecane-Water-Stearic Acid Phase-Change Nano-emulsions for Thermal Energy Storage" at the Experimental Nuclear Magnetic Resonance Conference (ENC) in Baltimore. Jay met jointly at the ENC with German collaborator, Dr. Ulrich Scheler, and PIRE co-PI Prof. Rob Messinger to discuss the NMR results on the phase-change nano-emulsions, as well as Ms. Park's future internship with Scheler at the IPF in Dresden, Germany.

PIRE Graduates

Manizheh Ansari

Fang Liu

Fanny Thomas

In 2019-2020 , the PIRE project graduated 3 Ph.D. students, Manizheh Ansari, Fang Liu & Fanny Thomas and 2 Masters student, Yamile Patino Vargas & Carlos Tavaras.

Yamile Patino Vargas

Carlos Tavaras

New Recruits

The PIRE project welcomes two new Ph.D. students, Moyosore Odunsi & Andres Velez Mendoza, & Masters student Rosanna Itrubide.

Andres Velez Mendoza
Thrust 3: Drilling Fluids

Moyosore Odunsi
Thrust 2: Gas Hydrates

Rosanna Itrubide
Modeling & Simulation

Fanny Thomas completed her Ph.D. thesis and graduated in April 2020. She now works in a Paris firm as a patent engineer specializing in fluids mechanics and the energy industries.

Capillary forces and wetting dynamics by diffuse-interface modeling

Wetting phenomena underlie many natural and industrial processes, from the proper functioning of the lungs to the thin coating of surfaces. The three-phase interactions involved at microscopic scales play a critical role. Adding solid particles to an emulsion, for example, can drastically change the flow behavior due to capillary bridging between the particles. The study of these three-phase systems is especially relevant to the petroleum industry, where gas hydrates forming large clusters in subsea pipelines during crude oil transportation is a major concern. The dynamics of such systems is also of great interest from a fundamental perspective. Indeed, describing non-equilibrium situations involving a 3-phase contact line is a long-standing problem that has never been explicitly resolved. The well-known moving contact line problem falls outside the scope of classical hydrodynamics and requires the use of approaches inclusive of both local phenomena and larger scale effects.

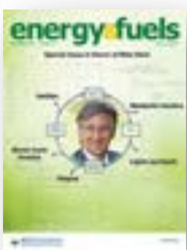
In the first part of this dissertation, the dynamics of capillary bridges and the motion of the three-phase contact line are studied within the framework of the diffuse interface theory. The key to understanding the dynamics of interfacial systems lies in an accurate description of the capillary forces. In this work, we combine the diffuse interface theory with a multiphase lattice Boltzmann algorithm to develop a description of the capillary forces in 2D binary systems. The forces and the surface tension are derived on a continuum level through the use of the capillary stress tensor. This approach provides a unified picture between fluid dynamics and thermodynamics, consistent with the multi-scale nature of the problem. The method is implemented for “pair" systems, composed of a liquid bridge connecting two solid elements. We identify the mechanisms governing the motion of the three-phase contact line and how the model handles the contact line singularity in comparison with the classic sharp-interface approach. We describe the two-way coupling between the dynamics of the solid elements and the fluid flow and discuss numerical challenges associated with moving curved boundaries, and the tracking of the interface. Numerical results are compared with theoretical predictions at equilibrium, and the capillary forces obtained in non-equilibrium situations are examined.

The interparticle forces due to capillary bridging depend on the wetting conditions of the solid surface. But these properties are not always well characterized: for example, the wetting characteristics of clathrate hydrates strongly influence their behavior in flow assurance situations, but direct experimental measurements are not prevalent in the literature. In the second part of this dissertation, a new experimental method is proposed for measuring the contact angle of various liquids on cyclopentane hydrate, a structure II clathrate hydrate that forms at atmospheric pressure. This method includes a protocol to obtain a smooth hydrate surface, followed by standard image-based contact angle measurements. The contact angle of halogenated organics drops immersed in brine is measured on cyclopentane hydrate and ice. Both the hydrate and ice surfaces are found to be water-wetting. Finite contact angles are obtained on the hydrate substrate but not on ice.

Recently Published Papers

"Liquid-Hexatic-Solid Phase Transition of a Hard-Core Lattice Gas with Third Neighbor Exclusion," S. Darjani, J. Koplik, S. Banerjee, V. Pauchard, J. Chem. Phys., **2019**, 151, 104702.

"Study of asphaltenes depositions onto stainless steel surfaces using quartz crystal microbalances with dissipation," F. Liu, S. Hickman, T. Maqbool, V. Pauchard, S. Banerjee, Energy & Fuels, **2020**, 34, 8, 9283-9295.



"Overview of Asphaltene Nanostructures and Thermodynamic Applications," B. Schuler, Y. Zhang, F. Liu, A.E. Pomerantz, A.B. Andrews, L. Gross, V. Pauchard, S. Banerjee, O.C. Mullins, Energy & Fuels, **2020**, 34, 12, 15082–15105.

"Effect of Interfacial Mass Transport on Inertial Spreading of Liquid Droplets," L. Baroudi, T. Lee, Physics of Fluids, **2020**, 32, 032101.

"Laboratory Evaluation of Static and Dynamic Sag in Oil-Based Drilling Fluids," T.N. Ofei, D. Kalaga, B. Lund, A. Saasen, H. Linga, S. Sangesland, R.K. Gyland. M. Kawaji, Society of Petroleum Engineers, **2020**.