1. Cover Sheet

In response to invitation for a proposal in "Partnership with College of Petroleum Engineering and Geoscience (CPG) at the King Fahd University of Petroleum and Minerals (KFUPM)."

Title: First-Principles Based Models, Methods, and Experiments on Reversible Shear Thickening Fluids for Drilling, Stimulation, Conformance Control, and EOR Operations

Proposing and Performing Institution: California Institute of Technology (Caltech), 1200 East California Blvd., Pasadena CA 91125, USA.

Subcontracting Performing Institution: Power Environmental, Energy Research Institute (PEERi), A California Non-Profit Research Organization, 738 Arrow Grand Circle, Covina, CA 91722, U.S.A. **Tel:** (626) 858-5077; **Fax:** (626) 858-9250; **Website:** <u>http://www.peeri.org</u>

Principal Investigator: William A. Goddard III, Charles and Mary Ferkel Professor of Chemistry, Materials Science, and Applied Physics and Director of the Materials and Process Simulation Center (MSC); Telephone: 626-395-3093 and 828-833-0036; email: wag@wag.caltech.edu and wagoddard3@gmail.com

Co-PI: Dr. Yongchun Tang, Director of Power Environmental, Energy Research Institute (PEERi), telephone: 626-695-4539; email: tang@peeri.org

Sr. Scientist: Dr. Andres Jaramillo-Botero; Director of Multiscale Simulations, MSC, Caltech; Telephone: 626-376-2432; email: ajaramil@caltech.edu

Sr. Scientist: Dr. Chengyang Jiang: Senior Scientist; PEERi, Telephone 626-858-5077; email: cyjiang@peeri.org

Proposed Budget: total over the three years: we are requesting a total of \$2,178,000 from KFUPM (annual budgets of \$753,000, \$710,000, and \$715,000).

Proposed Performance period: December 1, 2016 to November 30, 2019

I certify that the statements made in this proposal are true and complete to the best of my knowledge and that the Proposing Institution has authorized the submission of this proposal.

David J. Mayo, Director of the Office of Sponsored Research, Caltech; telephone 626-395-6219, Fax: 626-795-4571; email: david.mayo@caltech.edu

Signature: _____

Date:			

3. Executive Summary

We propose a collaborative research effort on polymer colloidal science applied to enhanced and improved oil recovery technologies (EOR/IOR), focused specifically on the application of unique first-principles based multiscale modeling and simulation methods, and novel experimental material synthesis and characterization capabilities, to: understand, validate, steer design, and optimize synthesis of smart nanopolymeric fluids for EOR/IOR.

The multiscale nature of our proposal enables us to develop improved understanding of the atomistic level mechanisms underlying shear induced modulation of viscosity of polymer fluids, and then to use this new understanding to design, synthesize, and validate new EOR/IOR fluids with controllable dynamic shear response.

The general expected outcomes include:

- 1. New multiscale simulation tools for simulating complex fluid phenomena
- 2. New validated materials providing controllable dynamic shear response
- 3. Improved research and education capacity on complex fluid phenomena at the CPG

More specifically, this effort will considerably enhance the fundamental understanding of the atomistic nanoscale mechanisms responsible for self-induced shear thickening/thinning in nano-fluid compositions applicable to EOR/IOR. We will connect "self-adaptive thickening" to fundamental atomic level information and will validate these new concepts with state-of-the-art rheological experiments relating nano-fluid compositions to the response to internal or external stimuli, including the electro-kinetic interactions of the fluid in porous media, and reversibility mechanisms and triggers. Thus, we will determine the correlation between the rheometer responses with the pressure-to-flow relationship in the porous media by using physical simulation in conjunction with numerical simulation. We expect to design "smart" polymer agent solutions that can be injected smoothly into the reservoir to penetrate much deeper into oil-bearing porous network. We expect to decrease additive concentrations to <1000 ppm while yielding a shear stress induced increase of ~ 100 times that of brines. In the moderate concentration levels (4000 ppm), such additives in fluids could further self-associate to significantly increase fluid viscosity for proppant carriers.

The key personnel: Goddard, Jaramillo-Botero, Tang, and Jiang bring more than 120 years of experience relevant to this project with expertise spanning fundamental theory, modeling, and experiments on complex polymer and nanoscale systems.

These advances should:

- 1. Put the CPG and their industrial sponsors at the forefront of developing the new generation of rheological fluids needed for EOR/IOR;
- Leverage the MSC-Caltech and PEERi technologies in coupling simulation and experimental into a closed cycle and integrating them to rapidly advance petroleum research;
- 3. Prepare a new class of researchers at KFUPM, Saudi Armco, and other partners capable of incorporating the continuing advances in simulation and materials technology relevant to EOR/IOR into the KFUPM curriculum and into industrial practice.

4. Project Description

4a Vision and Rational

This proposal focuses on the design, characterization, optimization, and development of new generation reversible shear-thickening/thinning fluids for drilling, stimulation, conformance control, and tertiary or enhanced oil recovery (EOR), using fast-prototyping combinations of first-principles theory and simulation methods to design and predict structure, properties, and phenomena from MSC-Caltech and advanced experimental technologies from PEERi to synthesize, characterize, and validate nano-polymeric fluids for EOR/IOR flow modulation.

We will focus on researching and evaluating new cost-effective, smart polymer-based fluid additives that can (a) increase aqueous phase viscosity thereby lowering the wateroil mobility ratio and (b) selectively seal off a "thief" layer or a channel to divert water to oil-rich zones having relatively lower permeability. More specifically, these "smart" polymer agents will exhibit reversible shear thickening behavior within the range of shear experienced in the reservoir, while returning to the base fluid viscosity on reaching the high shear region of the injection and production wells. We term this behavior as "**self-adaptive reversible shear thickening**". In particular, we propose to develop such "smart" polymer fluid systems with application to the following areas of significant interest to Saudi Arabia, KFUPM and CPG:

- 1. Enhanced Oil Recovery (EOR) focus on water-soluble polyacrylamide (PAM) polymer structures in various salinity and temperature conditions, to elucidate the relationship and reactive mechanisms involved in shear thickening.
- 2. Conformance Control focus on the electro-kinetic processes of the associated polymer (fluid flow through solid matrix) as a function of changes in shear rate, including solvent composition effects.
- 3. Drilling, Cementing, and Completion (DCC) focus on developing high-temperature tolerant polymers that can effectively block high shear rate zones, and on understanding the interactions between polymers and solid surfaces in DCC fluids.
- 4. Hydraulic Fracturing and Stimulation focus on developing a multi-functional polymer, capable of reducing friction and the ability to carry proppants (e.g. a polymer matrix with a controllable "viscoelastic" property).

In order to maximize hydrocarbon recovery by using advanced "smart" polymer fluids in a cost-effective and environmentally friendly manner, it is essential to apply fundamental science to improve our understandings on the interactions of the fluid with oil/gas and the rock matrix. Optimizing chemical performance under various reservoir conditions demands molecular-level modification of chemical products and fluid properties. To achieve these goals during this three year program, we will extend the breakthrough modeling and simulation technologies developed by the MSC at Caltech for *in-silico* design, characterization, and optimization of nanoparticle-based fluids. These breakthrough technologies include:

 Our new generation of high-accuracy quantum mechanics (QM) capable of describing electron correlation including London Dispersion (van der Waals attraction) from first principles (XYGJ-OS),[1, 2] with prediction of transition state barriers within 1.2 kcal/mol, and a fast universal way of correcting standard DFT methods for London Dispersion over the whole periodic table.[3] This will be fundamental to train largerscale simulation methods in our hierarchical multiscale strategy and for first-principles validation, without *a priori* availability of experimental data.

- 2. Our rule-based Universal Force Field (UFF)[4] to characterize the mechanics and conformational dynamics of crystalline and amorphous polymers blends as a function of shear and flow, including interaction with solvents and porous surfaces.
- 3. Our adiabatic ReaxFF reactive force field[5] based reactive molecular dynamics (RMD) methodology for describing reactive flows in large-scale systems (millions of atoms over 100's of nanoseconds) under equilibrium and non-equilibrium conditions with nearly the accuracy of QM, but at the cost of conventional force fields. ReaxFF has been validated and applied extensively to reactive fluids, fluid-solid interfaces, aqueous phase reactions[6] and surface chemistry, among others. It will be applied here to understand reactive fluid formation (synthesis and surface interactions), the electro-kinetics effects in the mechanical response of charged fluid flows in porous media, the relative tendency for charge distribution to be distorted by external electric fields (as triggering knobs for shear thickening-thinning), and dynamical polarization response (using a new polarizable charge equilibration (PQEq) strategy and the ReaxPQ extensions).
- 4. Our adaptive accelerated ReaxFF reactive hyper-dynamics method (aARRDyn)[7] to extend atomistic time scales in reactive modeling simulations with ReaxFF to time scales up to seconds (at computation costs corresponding to nanoseconds), and to understand nano-fluid interactions with hard rock and soft surfaces relevant to EOR/IOR,
- 5. Our ability to couple ReaxFF/ReaxPQ to large-scale dissipative particle dynamics (DPD) models, from training molecular fragments at the atomistic ReaxPQ level and derive the DPD parameters needed for coarse-grain DPD simulations will be used here to characterize the nano-fluids dynamic shear response mechanisms to endogenous and exogenous stimuli,
- 6. Our two phase thermodynamic (2PT) method[8-10] for accurately extracting entropy and free energy flow information from short dynamics simulations will be used to identify nano-fluid compositions that meet the target reversible shear-thickening response (the activation and magnitude of the shear-response mechanisms) from pico-sec dynamic simulations, and
- 7. Our multi-objective parameter optimization framework, GARFfield,[11] for systematic optimization of parameters in higher-than-QM scale methods (for ReaxFF/ReaxPQ and others) using diverse high accuracy QM data sets.

Additional details on these technologies and their capabilities are provided in the Supplemental Information (SI).

4b. Strategy for Success, work plans

Our strategy for success is based on coupling the unique first-principles predictive modeling and simulation capabilities for in-silico design, characterization and optimization at the MSC-Caltech, with the experimental synthesis; characterization; and validation capabilities at PEERi, and the research potential capabilities at KFUPM/CPG to address open problems with KFUPM industrial partners. The unparalleled technical strengths of the MSC-Caltech/PEERi team for novel polymer design, synthesis, characterization and application of shear-thickening/thinning nano-fluid formulations for EOR/IOR will be

transferred and enhanced by the participation and expected interactions with students, postdocs and Faculty from KFUPM/CPG.

Nowadays, water flooding remains the most commonly used oil recovery method, yet its efficacy is inevitably limited. The main reason for this is the inability to control the breakthrough of water in high permeability regions, commonly referred to as "poor conformance". In other words, the injected displacing fluid preferentially flows through the most permeable zones of reservoir thus leading to the premature breakthrough of the displacing fluid at the production well. Consequently, the injected fluid will bypass the remaining oil region without sweeping out the oils. Therefore, improving volumetric sweeping efficiency (VSE) has been considered as an essential factor in the success of any water flooding or EOR/IOR project. Polymer flooding is one of the relatively welldeveloped technologies that have been successfully commercialized for improving VSE in some of the giant oilfields. When conducting polymer flooding, partially hydrolyzed polyacrylamide (HPAM), a high molecular weight and viscosity-enhancing polymer, is added to the injected water to reduce the mobility of the water fluid and consequently improve the sweep efficiency. However, it has been found that the performance of polymer flooding can be substantially inhibited by the permeability variation between layers and within layers. That is, the HPAM polymers can only provide viscous enhancement (as a fluid viscosifying agent, FVA) but cannot divert fluid the oil-rich lowpermeability zones (as a fluid diverting agent, FDA).

In contrast to regular polymers, our single component "self-adaptive reversible shear thickening" polymer additive provides a distinct behavior with both FVA and FDA features. The introduction of such "smart" fluid technology, risk mitigation incentives and reducing chemical costs would enhance IOR/EOR economically in harsh circumstances. For instance, compared to traditional polymer flooding, the "smart" fluid flooding can be more applicable to complex reservoirs with either large well spacing or severe heterogeneity.



Figure 1. Schematic diagram of a subterranean oil-bearing reservoir from injection to production well, connected via a number of low-permeable (low k) and high-permeable (high k) zones/channels (left). And the flow profiles of injected fluids without conformance control (red) and with conformance control (green). The more uniform flow profile reduces the possibility of the early water breakthrough.

We expect the "smart" polymer fluid will to show shear thickening properties within the range of shear experienced in reservoirs, but return to the base fluid viscosity when reaching the high shear regions of the injector and producer (Figure 1). To attain this essential fine control of the rheological behavior of the "smart" polymer at the molecular level we must build up an in-depth understanding of the molecular scale interactions among various polymer functional groups the polymer backbone, structure, distribution and fraction of hydrophobic groups all will play key roles in achieving this adaptive rheology. Most important, is that we must also establish the correlation between rheometer response and flow behavior in porous media, because the rheological properties of the polymer solutions measured by conventional laboratory instruments that

produce pure shear flow will not be sufficient to predict the pressure-to-flow relationship in porous media. It is also critical to improve our understanding of the interaction of polymer with hydrocarbons and the rock matrix.

In a polymer solution, the viscosification is usually achieved by ultrahigh molecular weight, chain/coil expansion, or/and intermolecular 3D network in solution. The additive of functional polymers has drawn a great deal of attention both for its salinity tolerance and mechanical stability properties, and also for the unique rheological properties induced by the intra/inter hydrophobic interactions. For hydrophobic group modified HPAM, intra-molecular interactions are dominant at ultra-low shear rates. Shear thinning was first observed as the shear stress facilitating coil stretching along the shear direction. Further increasing the shear stress then triggers the transition from intramolecular association to intermolecular association and consequently the formation of 3D network macromolecular structure. This unique shear-thickening phenomenon is provided as a result of this network formation.

Extensive modeling and laboratory work has been carried out to determine the shear thickening mechanism of the semi-dilute entangled polymer solution. While a comprehensive molecular picture remains elusive, the shear thickening/thinning is interpreted through dynamic processes of dissociation of the associative cross-linkers. It has been proposed that the steady shear behavior for networks with different cross-linker is a result of a competition between two time scales – the average time of a cross-linker remains open (τ_0) and the relaxation time of a segment of the polymer chain (τ_s) (Figure 2). In the steady state, the association/cross-linking of hydrophobic groups is in a dynamic equilibrium in which the dissociation rate equals the association rate. When external forces are applied, e.g., the shear rate fluctuations, the time scale for the bonding will also change. When τ_0 is much larger than τ_s , the intermolecular association will be favored which leads to formation of a 3D network and shear thickening of the solution. When τ_0 is smaller than τ_s , the intramolecular association will be favored. Whereas τ_s is significantly affected by the external conditions, τ_0 is considerably an intrinsic property of polymer, which can be modified by changing its molecular structure and functional groups.



Figure 2: Schematic diagram of the exchange between intra-molecular to inter-molecular bonding of polymers. Scenario 1: intra-chain crosslinking when $\tau_0 < \tau_s$. Scenario 2: inter-chain crosslinking for $\tau_s < \tau_o$.

The shear-thickening polymers find many important uses in oilfield operations, such as drilling, cementing and stimulation. A variety of leakage pathways existing in reservoirs can lead to severe fluid loss during drilling or cementing operations, resulting in higher

production cost and even the failure of the construction projects, not to mention that severe environmental and formation damage could occurs if significant amounts of the drilling/cement fluids leak out to make contact with the local ground water systems. It is highly desirable for drilling and cementing operations to develop a "smart" polymer which maintains both the rheological and chemical behaviors of the working fluid upon addition while also providing fluid loss control (via the increase of viscosity, for instance) when encountering a range of geological leakage pathways

Hydraulic fracturing has become a most important technology, and is responsible for the recent boom in unconventional shale developments in North America. The shearthickening synthetic polymer offers a great opportunity to become a dual-function agent in the hydraulic fracturing operation, a novel technology known as S2X that is being developed by PEERi. That is, under the high shear rate pumping "slick water" condition, a low-concentration synthetic polymer is used as a friction reducing additive to reduce energy consumption from pumping; whereas at relatively lower shear rate "gelling fluid" condition, the same polymer chemicals (with increasing concentrations) possess significant shear-thickening viscosity, so that they act as the proppant carrying gelling agent (ideally, without additions of crosslinkers).

For these applications, polymer gel systems are formed either via crosslinking agents (preformed or *in-situ* formed) or via self-association under control of salinity, pH, temperature and pressure. Therefore, the fundamental understanding of the interaction of the polymer with other additives such as cationic species or surfactant components, and different types of rock surfaces (such as sandstone, dolomite, carbonate, clay, diatomic, etc.) is essential for selection and optimization of the polymeric materials.

This unique "self-adaptive viscosity modification" is most promising for application of EOR conformance control. Here the polymer solution will beneficially block the high permeability zone due to the thickening induced by the high shear rate, along with a number of advanced features in oilfield operations; there remain several technical hurdles to be addressed before application to production. To optimize the control of the rheological behavior in the solution, one must combine molecular design knowledge with skillful synthesis techniques. The polymer backbone, functionalized hydrophobic group structure/distribution/percentage will play an important role in the adaptive rheology. Although PAM-based modified polymers have been studied extensively, no systematic approach to manipulating and tuning the structure has been found. Most importantly, proficiency of PEERi in polymer synthesis techniques provides a large pool of "smart" polymer candidates that we can screen and characterize.

A major obstacle for applying "smart" polymer fluid technology is the lack of in-depth understanding of how rheometer response is correlated with flow behavior in porous media. Indeed, it is most likely that the optimum practical candidate for a self-adaptive polymer-based agent for in-depth conformance control remains to be discovered. This is why we have chosen the systematic study of polymer structure and rheology relationships, and the flow behavior of self-adaptive polymer-based agents in porous media, as the topic of this project.

To address the issues set forth above, we propose an R&D program combining strong teams of diversified multi-disciplinary expertise. We have assembled a program that integrates academic research with targeted industrial applications that will address the EOR/IOR challenges to find innovative and cost-effective solutions. The world-renown

chemical theory and molecular modeling carried out at MSC/Caltech offers essential insights and basic understanding of the bulk and interfacial molecular interactions of novel polymers/matrices prior to synthesis and characterization to provide *in silico* design. while, PEERi provides the expertise for conducting systematic laboratory synthesis and characterization of various "smart" polymers to test and evaluate the flow behavior in porous media by combining physical (core-flooding) and numeric (history-matching) simulations. These theoretical and experimental results will be combined to provide a unique, well-validate methodology, known as the quantitative structure-activity relationships (QSAR) and quantitative structure-property relationships (QSPR), to optimize the molecular structure of complex polymer-based agents with optimum efficiency. The studies we propose in this program are aimed to quickly identify the key challenges in self-adaptive thickening technology to allow the research team to rapidly reconfigure R&D activities so as to have the maximum possible impact in EOR/IOR.

Specifically, our theoretical modeling efforts will target finding answers to several important challenges to allow our laboratory studies to focus on the most promising optimal "smart" polymer fluids:

- Establishing an informative database of relaxation times τ₀ and τ_s of functionalized polymers with a variety of monomer additives, molecular weights, hydrophobicity's hydrophilicities, degrees of hydrolysis, charge densities, and glass transition temperatures to be used for developing QSAR/QSPR correlations with results determined from laboratorial tests.
- 2. Theoretical studies of the crosslinking mechanism of the developing "smart" polymers, with and without the presence of selective crosslinkers, such as borates and metallic compounds (Cr³⁺ or Zr³⁺), etc. Determination of the preferred binding site and binding energy of formation of nano-scale polymer network and gel formations. We will also consider the effect of salinity and hardness (divalent cations) of brines.
- 3. Viscosity and phase behavior prediction models of the "smart" polymer fluid system will be established with the focus on understanding the controlling factors involving molecular structure modifications on their rheological properties.
- 4. Interactions of the "smart" polymers with a variety of rock surfaces commonly encountered under typical reservoir conditions (sandstone vs carbonate) will be studied. This will include theoretical determination of the physical and chemical adsorption of polymers on the surfaces.

In conjunction with our theoretical programs, our experimental arm, PEERi, will conduct a series of novel experiments aimed at providing protocols and performance criteria to calibrate and validate our theoretical models.

- 1. A number of polyacrylamide (PAM) based functionalized polymers will be synthesized by combining monomers with different selectivities. After synthesis, we will utilize our Anton Paar MCR 302 Rheometer to measure their rheological properties, including G' (elastic behavior) and G" (viscous behavior). We will also conduct UV and NMR analyses for the polymer candidates exhibiting potential for further investigations.
- 2. Formation of the polymer gels with/without crosslinking agents (borates or metallic) of the "smart" polymers will be tested, under various combinations of polymer concentration, salinity, and temperature. For systems without crosslinking agents, we will also determine the critical association concentration (CAC) of the "smart" polymers.

- 3. We will use the Anton Paar Rheometer to determine the rheological properties for various concentrations of the "smart" polymer fluids under typical ranges of conditions experienced underground, such as shear rate 0.1 ~ 200 s⁻¹, from room temperature to up to 85 °C (185 F), and water salinity and hardness.
- 4. We will use both static and dynamic adsorption methods to determine the Interactions of the developing polymer solutions with various rock surfaces. Static adsorption experiments are useful in the initial screening studies, especially when there are large sets of candidate solutions for testing. However, dynamic sand column and/or core flooding experiments are essential to determine the hydrocarbon recovery potentials and economic factors of the "smart" polymer flooding.

Our proposal will develop improved understanding of the atomistic level mechanisms underlying shear-induced modulation of viscosity, and the design, synthesis and validation of new fracking fluids with controllable dynamic shear response. To this end, the team's work plan is summarized in Table 1 and detailed below.

Task	FY1				FY2				FY3			
Description	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Selection and												
optimization of force												
fields for MD simulations												
Nano-fluid model												
structure preparation,												
optimization and												
validation												
In-silico search,												
characterization and												
optimization of nano-												
fluids												
Synthesis of best												
performing <i>in-silico</i>												
predicted polymer												
candidates												
Experiments to												
understand and validate												
self-induced shear												
thickening/thinning												
Characterization of the												
atomistic dynamics flow												
behavior												
Characterize effects of												
nanoparticle size and												
character on properties												
Determine effect of												
continuous phase												
viscosity, temperature vs.												
type, rate, and time of												

deformation on shear						
rate for best performers						
Propose, synthesize and						
demonstrate one new						
nano-fluid for EOR/IOR						
Field case studies						

Table 1 Gantt chart describing the major tasks and their sequence in 3 years

FY1

1. Selection and optimization of force field parameters from QM datasets using the GARFfield framework for use in screening materials interactions, including monomers with a variety of functional units (including acrylamide, acrylic acid, biopolymers, and super-absorbent variants) and nanoparticles of SiO2, TiO2, CeO2, ZrO2, Al2O3, CaCO3, MgO, carbon nanotubes (CNT), and dendrimer-based.

• MSC-Caltech members will train, guide and collaborate with CPG members in the development of new high-accuracy first-principles force fields (e.g. Reax/ReaxPQ); from QM calculations on diverse training datasets needed to optimize atomistic reactive/non-reactive and coarse-grain force fields, to their validation

2. Model structure preparation, optimization and validation using QM optimized monomer units, QM-based force fields, and coarse-grain force fields of targeted structures (crystalline and amorphous polymers with embedded nanoparticles, cross-linking agents, in solvent, etc.).

• MSC-Caltech members will train, guide and collaborate with CPG members in preparing optimized, equilibrated and relaxed atomistic/coarse-grain model structures/compositions for high molecular-weight, water-soluble polymeric and nanoparticle based compositions and in performing validations against existing mechanical, rheological and thermo-dynamical theoretical/experimental data

3. Computational characterization studies to understand the nano-fluid rheological, mechanical and thermodynamic properties, under various reservoir conditions (brine pH, salinity, temperature, pressure, and other chemical additives) for *in-silico* screening of to find the best performers. This will include large-scale (millions of atoms), long-term (>microseconds) MD/RMD/aARRDyn/MC/DPD simulations and determining entropy and free energy from short 20 ps trajectories using 2PT to characterize equilibrium and non-equilibrium properties associated with rheological changes in screened fluid compositions over a realistic range temperatures and pressures.

• MSC-Caltech members will train, guide and collaborate with CPG members in performing large-scale computational experiments to characterize mechanical and thermodynamic properties of new systems using its latest multiscale methods and extensions (ab initio MD/RMD/aARRDyn/MC/DPD/2PT). This will include understanding how to couple QM to continuum models through predictable physical parameters. See SI for further details.

4. Organic synthesis of best performing i*n-silico* predicted polymer candidates, and systematic rheological studies to understand the Couette rheometer response and rheological properties, under various reservoir conditions (brine pH, salinity, temperature, pressure, and other chemical additives).

• PEERi members will train, guide and collaborate with CPG members in performing experimental protocols required to validate in-silico predictions

FY2

5. Theoretical and experimental effort to specifically understand and validate the underlying mechanisms in self-induced shear thickening/thinning at the atomistic/molecular levels.

• MSC-Caltech and PEERi members will train, guide and collaborate with CPG members in elucidating the conformational, compositional, and dynamical queues that lead to improved shear-thickening/thinning response (e.g. hydroclustering, order-disorder transitions, dilatancy, changes in stress regimes, surface tension, etc.)

6. Characterization of the atomistic dynamics flow behavior of best performing compositions and structures, within nano-porous media, including relating the onset of instabilities in the flow profile and the variations in shear and normal stress differences with changes in viscosity, exploring the dependence of the critical shear rate on the state points to be studied, characterizing the short-time mobility of the fluid particles and the deformation due to the applied shear, examining the microstructural changes and the probable formation of clusters accompanying any transition, as well as order-disorder transitions or dilatancy, and extensive core-flow experiments to mimic the field application conditions encounter in subsurface reservoirs.

• MSC-Caltech and PEERi members will train, guide and collaborate with CPG members in determining the sensitivity of the design parameter space to nanoparticle diffusion, fluid flow electrokinetics, and "smarter" knobs in multi-functional polymers that respond *in situ* to other types of stimuli in addition to shear stress (e.g. ionic strength, pH or temperature)[12] using molecular and fluid dynamics modeling.

FY3

7. Investigate effects of nanoparticle properties (e.g. size, shape, surface charge) and their concentration, distribution, interaction and volume fraction on the onset of shear-thickening/thinning, reduction in interfacial surface tension (disjoining pressure isotherm), and any potential alteration in rock wettability.

• MSC-Caltech members will train, guide and collaborate with CPG members to establish the performance dependence on particle sizes and distribution in fluid, the effect of electrostatics in particle interaction-induced friction forces, amphiphilicity for reversible shear-induced gelation in solvent, and interfacial conditions using the computational tools and techniques developed at the MSC (see SI).

8. Investigate how continuous phase viscosity, temperature, and the type, rate, and time of deformation affect the critical stress and shear rate at onset of shear-thickening/thinning on the best performing compositions. Elucidate and conclude on the dominant structural, compositional, chemical, and mechanical properties that lead to self-induced shear-thickening/thinning fluids.

• Collaborative research between MSC-Caltech, PEERi and CPG.

9. Propose, synthesize and demonstrate at least one nano-fluid composition for EOR/IOR that outperforms existing state of the art technologies.

• Collaborative research between MSC-Caltech, PEERi and CPG.

10. Field case studies against reservoir simulation and history matching modeling to provide scientific ranking of designed "smart" polymer fluids in actual oilfield operations. • Collaborative research between PEERi and CPG.

4c. Students, postdocs

This project would have several benefits to KFUPM, including:

1. The research programs would be directed to problems in oil and gas production relevant to KFUPM and its partner Saudi Aramco's interests, with the primary focuses on the fundamental science of interfacial phenomenon and complex fluid physics.

2. Caltech and PEERi would provide the means for KFUPM to build a core of experts, in theory, molecular simulation, novel laboratory design, and analysis, as well as experienced in applying these methods to solve tough industrial problems, which could then establish within KFUPM an effective organization and programs dedicated to applying these methods to the important internal technical problems across all areas of interests to KFUPM and Saudi Aramco.

Specifically, we anticipate transferring gradually the technology for molecular design theory and application methods to KFUPM, through close collaborations and research on several target scientific aspects related to the colloid and interface science and polymer physics and their applications to improve hydrocarbon recovery from subsurface under different geological conditions. We expect some direct outcomes from this proposed project as follows:

- Upon the completion of the project, the assistance and guidance by MSC/Caltech and PEER personnel will establish at KFUPM state-of-the-art research programs combining theory and computation (multiscale simulation), experimental evaluation (chemical EOR and chemicals for well stimulations), and geochemical rock analysis (rock, oil, condensate and gas properties);
- During each year of the project, t several of KFUPM and Saudi Aramco personnel (up to 4 at one time) will be work directly in the research facilities of MSC/Caltech and PEER;
- During each year of the project, we anticipate 1 3 joint publications in high impact peer-reviewed journals and 1 - 2 presentations at international conferences, such as Society of Petroleum Engineering (SPE) and International Petroleum Technology Conference (IPTC);
- During each year of the project, Caltech will hold an annual committee meeting to present technical progress and discussion. During this meeting, PIs and senior staff of Caltech and PEER will present their R&D progress of the previous year to the committee members and other KFUPM faculties and staffs. Future research directions and activities will also be discussed and decided during the meeting.
- We anticipate PIs and senior staffs of Caltech and PEER will serve as committee member of KFUPM graduate students to guide and assist their educational progress.
- Teleconference calls and group discussions will regularly take place among Caltech, PEER, and KFUPM members.

We envision that CPG personnel (faculty, staff, postdocs and students) would be closely coupled to MSC/Caltech and PEERi activities in this program. To that end, key personnel from CPG would be encouraged to intern at both facilities on an ongoing basis, and to actively participate in selected R&D programs at the theoretical modeling or experimental design/execution levels. CPG interns would be invited to participate in the MSC-Caltech weekly seminars (http://hokusai.wag.caltech.edu/pub/Main/GroupMeeting.html), and in its yearly research conference (http://www.wag.caltech.edu/anmeeting/), on specific topics of interest to this collaboration. We envision that the PIs and senior scientists from MSC/PEERi would visit

KFUPM/CPG to offer short-term courses, lectures and seminars on a yearly basis. These

will offer added opportunities for MSC-Caltech and KFUPM/CPG students to interact in state of the art research, relevant to this program. Furthermore, PIs from MSC/PEERi will also help and assist in building joint research programs and laboratories at KFUPM/CPG for enabling technology transfer and continued local research, as well as offering their scientific expertise on identification and selection of advanced research topics, undergraduate and graduate courses and programs for KFUPM/CPG, in particular on the emerging science, technology and applications in EOR/EIR. Visiting students from KFUPM/CPG will be encouraged to audit selected courses at Caltech, and to participate in the day-to-day research activities associated with this program. Courses offered by MSC-Caltech include the nature of the chemical bond (CH120 at Caltech), Atomic Level Simulations of Materials and Molecules (CH121 at Caltech), which cover such topics as Multiscale, Multiparadigm Modeling and Simulation, and Nanoscale Science and Engineering.

4d. Collaboration with Industry

The proposed project is targeting at large or medium-size oil operators, such as Saudi Aramco, who manage oil production from mature oilfields. Our proposal includes the nonprofit organization PEERi, directed by Dr. Yongchun Tang, which for 20 years has been quite active in conducting technology development, transfer and commercialization in the energy and environmental sector. Started by staff who left the Chevron Technology Corporation in 1999, PEER served as a partner research laboratory associated with MSC-Caltech for 9 years, and as PEERi has been an independent research nonprofit institute for 7 years, focusing on developing and commercializing energy-related technology for major oil producers and energy service companies. We anticipate that for the innovative technology emerging from this KFUPM project, PEERi could help facilitate application into the oil production market to benefit the energy production industry.

The "smart" polymer fluids developed in the project are expected to have significant direct industrial impact as replacement for the fluid now widely used in regular polymer flooding in EOR operations. Moreover, we propose to develop correlations between rheometer responses in the lab with the pressure-to-flow relationships in porous media by using physical stimulation (core flooding) in conjunction with numerical simulations. With well-calibrated rheological properties, the "smart" polymer fluids in hand, we can apply them under actual reservoir conditions in porous networks. Considering that the current HPAM-based polymer flooding often has poor oil recovery efficacy (average, 7% OOIP), we anticipate an additional 5 ~ 10 % OOIP oil recovery can be achieved by using the "smart" polymer fluid, without adding significant operation costs (single-component additive) and materials cost (10%). Consequently, successful demonstration of "smart" polymer fluids for EOR in this project could gain fast market acceptance by oil production companies, who currently use regular HPAM-polymer flooding as their tertiary oil recovery methods.

4e. Organization and Infrastructure

The material and process simulation center (MSC) at California Institute of Technology (Caltech) will partner with the Power Environmental Energy Research Institute (PEERi) for this project. Since 1990, Caltech's MSC (with 40+ active members) has developed unique methods for first principles multiscale, multi-paradigm prediction over a broad range of materials (ceramics, semiconductors, polymer, metal alloys, electrolytes, clays, etc.) the bulk structures, surface structures, static properties, and dynamic properties and phenomena. The MSC has applied these methods to understand and optimize the development of EOR-related technologies including material interfacial properties, surfactants, polymer systems, reactive fluids, nanoparticles and other oil field chemicals. PEER was established in 1999 as a research center (the PEER center) within the MSC at Caltech dedicated to improve the world's access to energy while minimizing environmental impact. In 2009, PEER became an independent research institute

in order to focus on technology collaboration and commercialization. Today, a total of 27 PhD Staff members work at PEER on various projects related to oil and gas research.

The PI, William A. Goddard III, Charles and Mary Ferkel Professor of Chemistry, Materials Science, and Applied Physics, is the Director and founder of the Materials and Process Simulation Center (MSC). He is a pioneer in creating, developing and applying ab initio methods to engineering applications. As PI he will be responsible for all aspects of the project. As Director of the MSC (with 30-40 postdocs and graduate students in computation and theory), he can call upon a large expert staff to help solve any technical problems as they arise. Goddard, has considerable experience leading multifaceted organizations that carry out fundamental research to solve complex multiscale systems. Goddard founded the Materials and Process Simulation Center (MSC) in 1990 to use atomistic approaches to solve industrial materials problems. Over 50 industrial companies have funded the MSC, with additional funding from essentially all US government research organizations. He developed a Light-Touch management style characterized by agile and adaptive leadership in which several senior managers responsible for specific areas work together to develop and bring appropriate methodologies to bear on complex problems solved. Prof. Goddard (PI) will oversee the collaboration with KFUPM and the work from all members involved in it.

Co-PI, Dr. Yongchun Tang, has more than 20 years of industrial experience in the area of petroleum chemistry (formerly a part of the Chevron natural gas management team) and 10 years of academic research and project development experiences. Since the departure from Chevron in 2000 after more than 12 years of R&D activities, Dr. Tang joined Caltech to establish the PEER center and served as the director to develop extensive R&D program in oilfield chemicals and their EOR/IOR applications, especially combining the advanced molecular simulation with the novel experimental design. He is a consultant in natural gas technologies for Shell, BP, Saudi Aramco, Chevron, and ConocoPhillips. Dr. Tang has also published more than 100 papers focusing on chemistry in oil & gas exploration and development. Also, he is the IP owner of the functional polymeric surfactant (FPS) and adaptive self-thickening polymer for EOR applications.

Co-PI, Dr. Andres Jaramillo-Botero is Director of Multiscale Simulation at MSC, Caltech. He is an expert in modeling and simulation of large-scale, long-term dynamics of materials and systems, involving multi-physics and scale-bridging algorithms. He leads the development and application of novel methods for non-adiabatic dynamics, which bridge quantum mechanics to molecular dynamics, for systems with millions of explicit electrons, coarse-grain force fields with constrained molecular dynamics methods, which connect the atomistic MD to the mesoscale, for long-term conformational search (ideal for characterization of polymers), and multiparadigm coupling using numerical optimization. He is an expert time-lower-bound algorithm development for massively parallel computations. Dr. Jaramillo-Botero will lead the first-principles modeling and simulation work in the partnership, and oversee the daily progress for corresponding graduate students and post-doctoral members of the collaboration.

Dr. Chengyang (Raymond) Jiang obtained his B.S. degree in chemistry from Peking University in China and his Ph.D. degree in materials chemistry from the University of Chicago. After serving as postdoctoral scholar in the Department of Materials Science and Engineering at University of California, Los Angeles, he joined the Power, Environmental and Energy Research (PEERi) Institute and is now senior research scientist. Dr. Jiang has a solid background in colloidal science, materials chemistry, nanotechnology and photovoltaics, with hands-on experiences working on several industry-sponsored research projects. These range from water treatment, thin film solar cells to oilfield chemicals. Dr. Jiang will lead the efforts for polymer synthesis and characterization from PEERi.

Dr. Le Lu received his Ph.D. degree in Petroleum Engineering from the University of Southern California. His expertise lies in history matching and basin modeling for applications in enhanced oil recovery (EOR), especially in the stochastic history matching, uncertainty quantification and data assimilation in reservoir characterization and production optimization. Dr. Lu will work on

evaluation and assessment of the oilfield applications of the "smart" polymer fluid system in EOR/IOR.

Dr. Di Zhu received his BS degree in Chemistry from Peking University and his Ph.D. degree in Material Chemistry from the University of Wisconsin at Madison. Dr. Zhu is a hand-on researcher who has been involved in a number novel experimental designs and laboratory testing procedures to evaluate and characterize specialty chemicals. Dr. Zhu will lead experimental programs from PEERi.

Our management philosophy to achieve success in this collaboration is:

- Integrate the theoretical and experimental studies; each effort provides validation and challenges to the results of the other. The net result is an efficient path to practical result with an improved basis for understanding. This approach has been applied successfully by us (Caltech/MSC and PEERi) for over 15 years. Our smooth working relationship makes it easier to achieve yet further improvements.
- 2. Provide the right mix of team members, both senior and young scholars, to bring a wide diversity of technical backgrounds and training. Our multidisciplinary views from both academic and industrial perspectives provide opportunities for creative approaches.
- 3. Integrate the fundamental, academic research expertise with participants from industrial research and chemical product development. In particular, recognize from the beginning, inputs from the industrial partners with regards to challenges that must be met to commercialize a process or a chemical product.
- 4. Frequent communication among project participants and up to date documentation.

We propose to organize an advisory committee composed of representatives of KFUPM, PEERi, Caltech and Saudi Aramco personnel to review, interact and provide annual guidance and advice on research progress and directions.

The teams at Caltech (Goddard and Jaramillo-Botero), PEERi (Tang, Raymond, Le and Di), and KFUPM/CPG (to be determined) will hold monthly meetings to discuss progress, milestones, problems, and opportunities. These will include:

- 1. Scheduled executive meeting (teleconference calls *via* Skype of WebEx) each month to discuss progress, milestones, problems, and opportunities;
- 2. Scheduled quarterly seminars open to all members of the partnership;
- 3. A wintertime all-hands technical meetings at Caltech at which progress on all aspects will be presented, and a summertime technical meeting at KFUPM to share results;
- 4. A web site restricted to team members will be created for communications of preliminary results in the form of presentations, rough draft manuscripts can also be shared; and
- 5. A web site open also to all partners having published and submitted papers available, along with theses. This will also have a schedule of seminars and meetings, etc.

5. Biographical Information

WILLIAM A. GODDARD, III

California Institute of Technology:

Charles and Mary Ferkel Professor of Chemistry, Materials Science, and Applied Physics Director of Materials and Process Simulation Center (MSC) MC 139-74; 1200 East California Blvd. Pasadena, California 91125 USA http://www.wag.caltech.edu / Phone: (626) 395-2731, FAX: (626) 585-0918 Email: wag@wag.caltech.edu, copy: shirley@wag.caltech.edu

Research Profile

Goddard has been a pioneer in developing methods for quantum mechanics (QM), force fields (FF), reactive dynamics (ReaxFF RD), electron dynamics (eFF), molecular dynamics (MD), and Monte Carlo (MC) predictions on chemical, catalytic, and biochemical materials systems and is actively involved in applying these methods to ceramics, semiconductors, superconductors, thermoelectrics, metal alloys, polymers, proteins, nuclei acids, Pharma ligands, nanotechnology, and energetic materials. A particular focus has been to determine the detailed reaction mechanisms underlying heterogeneous and homogeneous catalysts, including electrocatalysis. The goal of the Goddard research has been to develop the methods sufficiently accurate that the need for experimental validation can be severely restricted to the predicted best systems and sufficiently efficient that they can be applied to realistic systems with millions of atoms (now referred to as Materials Genomics). He uses hierarchical approaches (multiscale, multiparadigm) to couple between the electronic states of QM with dynamics of macroscale systems, enabling first-principles based accuracy of realistic systems (millions of atoms, millisecond time scales). The Materials and Process Simulation Center (MSC) that he founded and directs, has a critical mass of expertise in all these areas to improve the methods needed for this project and to train the students and postdoctoral fellows from KFUPM.

Education and Training:

- o Alfred A. Noyes Research Fellow of Chemistry, Caltech (Nov. 1964-Dec. 1966)
- o Ph.D. Engineering Science (minor physics), California Institute of Tech., 1965 (Oct. 1964)
- BS Engineering (Highest Honors), University of California, Los Angeles, 1960.

Research and Previous Professional Experience (all at Caltech):

2001-present. Charles and Mary Ferkel Professor of Chemistry, Materials Science, Appl. Phys. 1990-present. Director of Materials and Process Simulation Center (MSC)

- 1992-1997 Director of NSF Grand Challenge Applications Group at Caltech
- 1984-2001 Charles and Mary Ferkel Professor of Chemistry and Applied Physics
- 1984-1990 Director of NSF Materials Research Group at Caltech
- 1978-1984 Professor of Chemistry and Applied Physics

1967-1978 Assistant, Associate, and Full Professor of Theoretical Chemistry

Selected Awards and Honors (since 1984)

- o Elected Member of National Academy of Science (1984)
- o Elected Member of International Academy of Quantum Molecular Science (1988)
- o Elected Fellow of American Physical Society (1988)
- o Winner American Chemical Society Award for Computers in Chemistry (1988)

- Awarded Feynman Prize for Nanotechnology Theory (1999)
- Named ISI Highly Cited Chemist for 2001 (http://isihighlycited.com)
- Winner 2002 Prize Computational Nanotechnology Design (Inst. Molecular Manufact.)
- o Awarded American Chemical Society Award for Theoretical Chemistry (2007)
- o Elected Fellow of the Royal Society Chemistry (2008)
- o Awarded NASA Space Sciences Award for Space Shuttle Sensor (2009)
- Awarded NASA Space Sciences Award for polymer films (2012)
- Award Distinguished Scientific Achievement in Catalysis 7th World Congress Oxidation Catalysis (2013)
- Named ISI Highly Cited Chemist for 2014 (http://isihighlycited.com)
- Named ISI Highly Cited Chemist for 2015 (http://isihighlycited.com)
 Selected Recent Research publications: total over 1160 (H index = 127, I-10 index 937)
 https://scholar.google.com/citations?user=yMZIErUAAAAJ&hl=en
 http://www.wag.caltech.edu/publications/papers/
- Handbook of Nanoscience, Engineering, and Technology, Third Edition; William A Goddard III, Donald W. Brenner, Sergey E. Lyshevski, and Gerald J. Iafrate CRC Press Taylor and Francis Group, 2012; Print ISBN: 978-1-4398-6015-1; eBook ISBN: 978-1-4398-6016-8
- Tensile Strength of Liquids: Equivalence of Temporal and Spatial Scales in Cavitation; Cai Y; Huang JY; Wu HA; Zhu MH; Goddard WA & Luo SN; J. Phys. Chem. Lett., 7 (5): 806-10 DOI: 10.1021/acs.jpclett.5b02798 (2016)
- Phase stability in nanoscale material systems: extension from bulk phase diagrams; Bajaj S; Haverty MG; Arroyave R; Goddard WA & Shankar S; Nanoscale, 7 (21): 9868-9877 (2015)
- Non-adiabatic dynamics modeling framework for materials in extreme conditions; Xiao H; Jaramillo-Botero A; Theofanis PL & Goddard WA; Mechanics of Materials, 90 SI:243-252 (2015)
- Assessment of phenomenological models for viscosity of liquids based on nonequilibrium atomistic simulations of copper; Xu, P; Cagin, T; Goddard, WA; J. Chem. Phys., 123 (10): Art. No. 104506 (2005)
- Atomistic Characterization of Stochastic Cavitation of a Binary Metallic Liquid under Negative Pressure; An, Q; Garrett, G; Samwer, K; Liu, Y, Zybin, SV; Luo, SN; Demetriou, MD; Johnson, WL; Goddard, WA; J. Phys. Chem. Let., 2 (11): 1320-1323 (2011)
 Other Professional Activities:
- Consultant (at various times): General Electric, General Motors, Shell Development, Imperial Chemical Industry, BP, Exxon, Chevron, SOHIO, Dow Chemical, AT&T Bell Labs, Union Carbide, Celanese, Allied Signal, UOP, 3M, Proctor and Gamble, Dow Corning, Nissan, MSI (Accelrys), Schrödinger, Eidogen, Systine, PharmSelex
- Member, Board of Trustees Gordon Research Conferences 1988-1994
- Cofounder Molecular Simulations Inc. (now named Accelrys) (1984), San Diego CA. Member Board of Directors (84-95), Chairman Board (84-91)
- Cofounder Schrödinger Inc. (1990), New York City. Member Board of Directors 1990-2000; Chairman Scientific Advisory for Materials (2012-present)
- o Cofounder-AquaNano Inc Pasadena CA (2009), Chairman SAB (2009-present)

Dr. ANDRES JARAMILLO-BOTERO

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Researc		
Research Scientist	 California Institute of Technology (Caltech), Chemistry and Chemical Engineering division, Pasadena, California, United States. Director, Multiscale Science and Simulation at the Materials and Process Simulation Center (MSC). Lecturer in Chemistry. Atomic Level Simulations of Materials. Mentor/co-mentor. Postdocs and Ph.D. thesis in Chemistry, Materials Science, and Engineering; SURF and MURF (Summer/Minority Undergraduate Research Fellowship). 	6/2006- Present
Professor	 Pontificia Universidad Javeriana (PUJ), Engineering Faculty, Cali, Colombia. Professor (tenure in 1999), Electronics Eng. and Computer Science. Founding Director (PI), Robotics and Automation Research Group Founding Director, Process Automation technology transfer Center University Board Council member Faculty Engineering Dean (Youngest ever). Faculty+staff: ~300+. Student population: ~2,500 (2004) Chair Electronics Engineering and Chair Computer Science 	1/1990- 5/2006 1990-2006 1995-2006 1999-2004 1998-2004 1998-2004
Research Associate	 Caltech, Chemistry and Chemical Engineering, Pasadena, CA, United States. Host: William A. Goddard III. NSF funded fellow on Computational Nanotechnology. NSF Pan American Advanced Institute (PASI) on Molecular Engineering and Computational Nanotechnology program co-I and co-organizer. 	9/2004- 6/2005 8/2002-
NSF Fellow	Mathematics (IPAM), Los Angeles, CA, United States. Host: Mark Green. • Nanoscale Science and Engineering program.	8/2002- 12/2002
Invited Faculty Associate	Jet Propulsion Laboratory (JPL-NASA), Ultracomputing group, Engineering and Science Directorate, and Caltech, Chemistry and Chemical Engineering, Pasadena, CA, United States. Hosts: Fijany (JPL) and Goddard III (Caltech) o Constrained molecular dynamics modeling of nanoscale systems.	9/1996- 12/1997
Invited Researcher /Trainee	 Mechanical Engineering Laboratory (MEL), Autonomous Machinery Division, Robotics Department, Tsukuba, Japan. Ministry of Trade and Industry (MITI). Host: Katsuo Yamaba Fellow from the Advanced Industrial Science and Technology (AIST) and Japan Industrial Technology Association (JITA) in research/training on advanced robotic technologies. 	6/1992- 5/1993
Other	 Systems Engineer. Sistemas de Tecnología Avanzada, Digital Equipment Corporation (DEC), Cali, Colombia, and Electronic Control Systems Designer. Sincrón Diseño Electrónico Ltda, Cali, Colombia 	1-9/1988 12/86-12/87

Research and Professional Experience

Education and Training

- Doctor of Engineering (Industrial), Universidad Politécnica de Valencia (UPV), Valencia, Spain.
 1998. Outstanding *cum-laude*, ranked 1st in class.
- Master of Science (Computer Science), State University of New York (SUNY), Binghamton, New York, USA. 1989. Fulbright scholar.

- Bachelor of Science (Electrical Engineering), Boston University, Boston, Massachusetts, USA. 1986.
- International Baccalaureate High-level Degree Physics, International Baccalaureate Office, UK. 1982.

Selected Recent Publications

- Fortunelli, A., Goddard III, W.A., Sementa, L., Barcaro, G., Negreiros, F.R., Jaramillo-Botero, A., "The atomistic origin of the extraordinary oxygen reduction activity of Pt3Ni7 fuel cell catalysts", Royal Society Chem. Sci., DOI: 10.1039/C5SC00840A, 2015
- 2. Xiao, H., Jaramillo-Botero, A., Theofanis, P.L., Goddard III, W.A. "Non-adiabatic dynamics modeling framework for materials in extreme conditions", Mechanics of Materials, Elsevier, 10.1016/j.mechmat.2015.02.008, 2015
- 3. An, Q., Cheng, M.J., Goddard, W.A. and Jaramillo-Botero, A. "CCI Radicals As a Carbon Source for Diamond Thin Film Deposition", J. Phys. Chem. Lett., 2014, 5 (3), pp 481-484
- Cheng, T., Jaramillo-Botero, A., Goddard, W.A., and Sun, H. "Adaptive Accelerated ReaxFF Reactive Dynamics with Validation from Simulating Hydrogen Combustion", J. Am. Chem. Soc., 2014, 136 (26), pp 9434-9442
- 5. Jaramillo-Botero, A., Naserifar, S., and Goddard, W.A. "A General Multi-objective Force Field Optimization Framework, with Application to Reactive Force Fields for Silicon Carbide", J. of Chemical Theory and Computation, 2014, 10(4), pp 1426-1439
- Jaramillo-Botero, A., Qi, A., Cheng, M.J., Goddard, W.A. III, Beegle, L., and Hodyss, R., "Hypervelocity impact effect of molecules from Enceladus' Plume and Titan's upper atmosphere on NASA's Cassini Spectrometer from Reactive Dynamics Simulations", Phys. Rev. Letters (PRL), 109, 213201, 2012.
- 7. Jaramillo-Botero, A., Tahir-Kheli, J., von Allmen, P., Goddard WA III, "Multiscale, multiparadigm modeling for nano systems characterization and design", CRC handbook of Nanoscience, Engineering and Technology, 3rd ed. Chapter 29. In press (May 2012).
- 8. Liu, L, Jaramillo-Botero, A., Goddard, W.A. III, and Huan, S. "Development of a ReaxFF Reactive Force Field for Ettringite and Study of its Mechanical Failure Modes from Reactive Dynamics Simulations", J. Phys. Chem. A, 2012, 116 (15), pp 3918-3925.
- 9. Theofanis, P.L, Jaramillo-Botero, A., Goddard, W.A. III, Mattsson, T., Thompson, A. "Electron dynamics of shocked polyethylene crystal", Phys. Rev. B 85, 094109 (2012).
- Jaramillo-Botero, A., Nielsen, R., Pascal, T., Abrol, R., Mueller, J., and Goddard, WA III, "Firstprinciples-based multiscale, multiparadigm molecular methods for describing complex chemical processes", Topics in Current Chemistry, Volume 307, pages 1-42, (2012). Special issue on Multiscale Molecular Methods in Applied Chemistry, Ed. Kirchner, B, Vrabec, J, 307:1-42 (2012).

Synergistic Activities: *Significant contributor* to LAMMPS, Sandia's National Laboratory Large-scale Atomic/Molecular Massively Parallel Simulator; *Principal developer*, parallel electron force field and extensions (e.g. effective core potentials) user package in LAMMPS; *Principal developer*, GaRFField: hybrid evolutionary/gradient based optimization framework for (reactive and non-reactive) force fields; *Principal developer*, Robomosp: ROBotics Modeling and Simulation Platform (see sample sims: 7-DOF PA-10 kinematics, dynamics); *Principal developer*, CMDF: first-principles based Computational Materials Design Facility; *Lecturer and Invited speaker* at multiple academic/industrial institutions and national laboratories in U.S., Europe, and Latin America; *Peer project/paper reviewer* for: US Department of Energy – DOE; National Science Foundation – NSF; Institute of Electrical and Electronics Engineers – IEEE; International Federation of Automatic Control (IFAC); Iberoamerican program for science and technology for development (CYTED); Colciencias - NSF equivalent in Colombia; and several indexed journals.

Dr. Yongchun Tang

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PROFESSIONAL PREPARATION:

- o B.S. Chemistry, Shanxi University, China, 1981
- o Ph.D. Chemistry, Ohio University, 1985

APPOINMENTS:

- o Postdoc appoint at Harvard University, 1987-1988
- o Research Chemist at Chevron Technology Corporation, La Habra, CA 1988-1993
- Senior Research Scientist at Chevron Technology Corporation, Group Leader for Molecular Modeling, 1993-1999
- o Adjunct Professor at Cornell University, 1998
- Director of Power Environmental Energy Research Center at California Institute of Technology 1999-2009
- o Director of Power Environmental Energy Research Institute, 2009-present

SYNERGISTIC ACTIVITIES:

- o Founder and Director of Power Environmental Energy Research Center (PEER) at Caltech
- o Founder and Director of Power Environmental Energy Research Institute (PEERi)
- Co-Founder and Broad member of ChemEOR, GeoIsoChem, Paladin Logging, ArrowGrand, Tensiogreen, Aqpure and etc.
- Organized many international conference including best ACD symposium of Natural Gases, First AAPG Herberg conference of unconventional resource in Beijing, China and etc.

COLLABORATIONS AND OTHER AFFLIATIONS:

- Adjunct Professor: Beijing University (2008-present)
- Adjunct Professor: Green Chemical and Environmental Energy Research Institute, Shanghai University (2009-2013)
- Adjunct Professor, Geochemistry Institute of Chinese Academy of Science (2000-present)
- o Board Member of Invited Expert Committee for All-China Federation of Returned Overseas
- o Member of Oversea Scientific Advisory Board, CNPC Key Laboratory of Petroleum Geology
- Corporation Consultations for Chevron, Sandi Aramco, Shell, British Petroleum, Mobil, ConocoPhillps, China Petroleum Corporation (Taiwan), ENI-Apig, Petrobra and etc.

SELECCTED PUBLICATION:

- P. J. Shuler, Z. Lu, Q. Ma, Y. Tang. Surfactant Huff-n-Puff Application Potentials for Unconventional Reservoirs. SPE-179667-MS, the SPE Improved Oil Recovery Conference, Tulsa, OK, 11-13, April 2016
- Q. You, K. Wang, Y. Tang, G. Zhao, Y. Liu, M. Zhao, Y. Li, C. Dai. Study of a Novel Self-Thickening Polymer for Improved Oil Recovery, Industrial & Engineering Chemistry Research 2015, 54, 9667-9674
- 3. L. Co, Z. Zhang, Q. Ma, G. Watts, L. Zhao, P. J. Shuler, **Y. Tang**. Evaluation of Functionalized Polymeric Surfactants for EOR Applications in the Illinois Basin. Journal of Petroleum Science and Engineering **2015**, 134, 167-175.

- 4. Q. Ma, P. J. Shuler, C. W. Aften, **Y. Tang**. Theoretical Studies of Hydrolysis and Stability of Polyacrylamide Polymers. Polymer Degradation and Stability **2015**, 121, 69-77
- 5. W. Xia, Z. Du, Q. Cui, H. Dong, F. Wang, P. He, **Y. Tang**. Biosurfactant Produced by Novel *Pseudomonas sp.* WJ6 with biodegradation of *n*-alkanes and polycyclic aromatic hydrocarbons. Journal of Hazardous Materials **2014**, 276, 489-498
- 6. Q. You, **Y. Tang**, B. Wang. F. Zhao. Enhanced Oil Recovery and Corrosion Inhibition through a Combined Technology of Gel Treatment for Water Shutoff and Corrosion Inhibitor Huff & Puff in Oil Well. Procedia Engineering **2011**, 18, 7-12
- 7. P. J. Shuler, H. Tang, Z. Lu, Y. Tang. Chemical Process for Improved Oil Recovery From Bakken Shale. CSUG/SPE-147531, Canadian Unconventional Resources Conference, Calgary, Alberta, Canada, 15-17, November, 2011.
- 8. Y. Wu, S. Iglauer, P. J. Shuler, **Y. Tang**, W. A. Goddard, III. Alkyl Polyglycoside-Sorbitan Ester Formulation for Improved Oil Recovery. Tenside Surf. **2010**, 47, 280-287.
- 9. P. J. Shuler, **Y. Tang**, H. Tang, Heavy Oil Production Enhancement by Viscosity Reduction. SPE-132564, Western North America Regional, Anaheim, CA 26-30, May **2010**.
- 10. Y. Wu. S. Iglauer, P. J. Shuler, **Y. Tang**, W. A. Goddard, III. Branched Alkyl Alcohol Propoxylated Sulfate Surfactants for Improved Oil Recovery. Tenside Surf. **2010**, 47, 152-161
- 11. S. Iglauer, Y. Wu, P. J. Shuler, **Y. Tang**, W. A. Goddard, III. Dilute iota- and Kappa-Carrageenan Solutions with High Viscosities in High Salinity Brines. Journal of Petroleum Science and Engineering. **2011**, 75, 304-311.
- Y. Wu. K.S. Wang, Z. Hu, B. Bai, P. J. Shuler, Y. Tang. A New Method for Fast Screening of Long-Term Thermal Stability of Water Soluble Polymers for Reservoir Conformance Control. SPE-124257, SPE Annual Technical Conference and Exhibition, New Orleans, LA, 4-7, October, 2009
- Y. Tang, P. J. Shuler, S. K. Cheug, J. A. Goodgame, J. J. Hsu, A. V. Padilla Improved Transportation of Waxy Crude Oils and Emulsions in Bakasap Area, Indonesia. SPE-80243 SPE International Symposium of Oilfield Chemistry, Houston, TX 5-8 February, 2003.
- 14. K.S. Wang, R. Resch, K. Dunn, P. J. Shuler, **Y. Tang**, B. E. Koel, T. F. Yen. Scanning Force Microscopy Study of Etch Pits Formed during Dissolution of a Barite (001) Surface in CDTA and EDTA Solutions. Langmuir, **2000**, 16, 649-655

PATENTS AND APPLICATIONS

- o R. Zhang and **Y. Tang** (2015) Functional Polymer for Enhanced Oil Recovery, US 9,023,966
- Y. Tang, H. Tang, P. He (2015) Hydrocarbon Recovery Dispersions. US Applications 20150075798
- **Y. Tang**, W. Zhou (2014) Using Methanesulfonyl Halide as a Key Intermediate for Methane Gas to Liquid Conversion and Raw Commodity Chemical Generation. US 8,916,734
- S. Wu, A. Deev, Y. Tang (2013) Sensor System Using a Hollow Waveguide. US Application 20130058830
- o S. Wu, A. Deev, S.L. Palm, Y. Tang, W.A. Goddard, III (2010) Optical Gas Monitor, US 7,843,565
- Z. Li, **Y. Tang**, J. Cheng. (2009) Use of Ionic Liquids as Coordination Ligands for Organometallic Catalysis, US 7,615,644
- S. Wu, Y. Tang, (2008) Dark-Field Laser-Scattering Microscope for Analyzing Single Macromolecules. US 7,365,835
- Z. Li, **Y. Tang**, J. Cheng (2008) Stable Ionic Liquid Complexes and Methods for Determining Stability Thereof. Patent Application 20080214814
- **Y. Tang**, P.J. Shuler, Y. Wu, S. Iglauer (2006) Chemical System for Improved Oil Recovery, US Application 20060046948
- **Y. Tang**, W. A. Goddard, III, R. Periana (2005) Methods of Discovering or Developing Novel Materials and Molecules. US Application 20110166039

Chengyang Jiang, Ph.D.

Power Environmental Energy Research Institute

Education and Training

- Postdoctoral Scholar, Materials Science and Engineering Univesity of California, Los Angeles, CA, 2014-2015
- o Ph.D. in Materials Chemistry University of Chicago, Chicago, IL, 2013
- o M.S. in Chemistry University of Chicago, Chicago, IL, 2009
- o B.S. in Chemistry Peking University, Beijing, China, 2008

Research and Professional Experience

Research Scientist, Power Environmental Energy Research Institute (PEERi), Covina CA, 2015-now.

- Design and synthesize novel polymeric compounds for various oilfield applications.
- Develop new forward osmosis systems to treat production wastewater with high salinity.
- Develop high-throughput method to identify the maturities of source rocks.
- **Postdoctoral Scholar**, University of California, Los Angeles, Los Angeles, CA, 2014-2015.
- Led the development of novel chemistry for new generation solar cells, achieving 7.4% efficiency.
- Collaborated with scientists at BASF to solve key issues in fabrication of thin film materials.
- Mentored 2 graduate students to develop research plans, conduct experiments and interpret results.
- Participated in the research targeting high-performance hybrid solar cells.

Research Associate, the University of Chicago, Chicago, IL, 2014.

Doctorate Research Assistant, the University of Chicago, Chicago, IL, 2009-2013.

- Initiated solar cell research in the group by designing, synthesizing and characterizing a class of precursors for solution processing of thin films.
- Developed synthetic routes for high-quality semiconductor nanocrystals with plasmonic features, highlighting both new physics and applications in spectroscopy.
- Studied reaction and sintering mechanisms of various liquid-phase precursors. This work is fundamental to understanding of solid-state chemistry at nanoscale.
- Established thin film fabrication systems and standard operation procedures for blade and spray coating.

Baccalaureate Research Assistant, Peking University, Beijing, China, 2006-2008.

• Synthesized silver colloids for application in surface-enhanced Raman spectroscopy and superhydrophobic gold nanoarrays using colloidal lithography.

Publications

- Efficiency Enhancement of Cu₂ZnSn(S,Se)₄ Solar Cells via Alkali Metals Doping. Y.-T. Hsieh,* Q. Han,* <u>C. Jiang</u>, T.-B. Song, H. Chen, L. Meng, H. Zhou, Y. Yang. *Adv. Energy Mater.* 2016, DOI: 10.1002/aenm.201502386.
- Controlling Solid-Gas Reactions at Nanoscale for Enhanced Thin Film Morphologies and Device Performances in Solution-Processed Cu₂ZnSn(S,Se)₄ Solar Cells. <u>C. Jiang</u>, Y.-T. Hsieh, H. Zhao, H. Zhou, Y. Yang. *J. Am. Chem. Soc.* 2015, *137*(34), 11069-11075.

- Low-Impurity High Performance Solution-Processed Metal Oxide Semiconductors via a Facile Redox Reaction. H. Chen, Y.-S. Rim, <u>C. Jiang</u>, Y. Yang. *Chem. Mater.* 2015, 27(13), 4713-4718.
- 4. Perovskite solar cells: film formation and properties. T.-B. Song, Q. Chen, H. Zhou, <u>C.</u> Jiang, H.-H. Wang, Y. (M.) Yang, Y. Liu, J. You, Y. Yang. *J. Mater. Chem. A.* **2015**, *3*, 9032.
- Spatial Element Distribution Control in a Fully Solution-Processed Nanocrystals-Based 8.6% Cu₂ZnSn (S,Se)₄ Device. W.-C. Hsu , H. Zhou, S. Luo , T.-B. Song , Y.-T. Hsieh , H.-S. Duan, S. Ye , W. Yang , C.-J. Hsu , <u>C. Jiang</u>, B. Bob , Y. Yang. *ACS Nano* **2014**, *8*, 9164.
- Moisture assisted perovskite film growth for high performance solar cells. J. You, Y. (M.) Yang, Z. Hong, T.-B. Song, L. Meng, Y. Liu, <u>C. Jiang</u>, H. Zhou, W.-H. Chang, Y. Yang. *Appl. Phys. Lett.* **2014**, *105*, 183902.
- 7. The role of precursor reactivity in solution processing of thin film semiconductors: case of Cu₂ZnSnS₄. <u>C. Jiang</u>, W. Liu, D. V. Talapin. *Chem. Mater.* **2014**, *26*(13), 4038–4043.
- Vacancy-doped plasmonic copper chalcogenide nanocrystals with tunable optical properties. I. Kriegel, J. Rodríguez-Fernández, <u>C. Jiang</u>, R. Schaller, E. Da Como, D. V. Talapin, J. Feldmann. In *Ultrafast Dynamics in Molecules, Nanostructures and Interfaces*: Proceedings of the 7th International Conference on Materials for Advanced Technologies, Singapore, 2013; pp. 272-291.
- Isolable colloidal particle, useful in device e.g. printed circuit, photovoltaic cell, piezoelectric crystal, comprises an inorganic capping agent bound to a surface of a nanoparticle. D. V. Talapin, M. V. Kovalenko, J.-S. Lee, <u>C. Jiang</u>. WO2010124212-A3; EP2430112-A2; US2012104325-A1.
- Soluble precursors for CuInSe₂, CuIn_{1-x}Ga_xSe₂ and Cu₂ZnSn(S,Se)₄ based on colloidal nanocrystals and molecular metal chalcogenide surface ligands. <u>C. Jiang</u>, J.-S. Lee, D. V. Talapin. *J. Am. Chem. Soc.* **2012**, *134*(11), 5010-5013.
- Tuning the excitonic and plasmonic properties of copper chalcogenide nanocrystals. I. Kriegel,* <u>C. Jiang</u>,* J. Rodríguez-Fernández, R. Schaller, D. V. Talapin, E. Da Como, J. Feldmann. J. Am. Chem. Soc. 2012, 134(3), 1583-1590. (* shared first authorship)

Synergistic Activities

- Served as invited reviewer for the following journals: ACS Nano, Appl. Phys. Lett., Express Polym. Lett., Chem. Phys. Lett., Phys. Status Solidi A, Solid State Commun., J. Phys. Chem. Solids.
- 2016.02 Seminar Speaker: Shale Gas/Oil Joint Industry Partnership Meeting. Industry, CA.
- o 2013.10 Seminar Speaker: Postdoctoral Research and Career Symposium. Argonne, IL.
- o 2013.06 Seminar Speaker: 55th Electronic Materials Conference. South Bend, IN.
- o 2013.05 **Presenter**: 17th GLCACS Conference. Round Lake, IL. (2nd place in competition)
- 2013.04 Poster Presenter: Materials Research Society Spring Meeting. San Francisco, CA.

Dr. Di Zhu

EDUCATION

- o Sep.2010 Aug.2014 Ph.D. Chemistry, University of Wisconsin at Madison
- *Sep.2006 Jul. 2010* B.S., Chemistry (Minor in Economics), Peking University, China **HONORS AND AWARDS**

• **National Scholarship**, Ministry of Education of the People's Republic of China (2008) **RESEARCH EXPERIENCE**

2014-present Senior Scientist, Power Environmental Energy Research Institute

2010 – 2014 Research Assistant, Hamers research group (Professor Robert Hamers)

2009 – 2010 Research Assistant, Molecular catalysis research group (Professor Haichao Liu)

2007 - 2009 Research Assistant, Nuclear environment research group (Professor Chunli Liu) **PATENT AND PUBLICATIONS**

- Di Zhu, Linghong Zhang, Rose Ruther and Robert J. Hamers, Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction, Nature Materials, 12, 836-841, 2013
- Jeffrey R. Christianson , Di Zhu , Robert J. Hamers, and J. R. Schmidt, Mechanism of N2 Reduction to NH3 by Aqueous Solvated Electrons, J. Phys. Chem. B, 118(1), 195-203, 2014
- Linghong Zhang, Di Zhu, Gilbert M. Nathanson and Robert J. Hamers, Selective Photoelectrochemical Reduction of Aqueous CO2 to CO by Solvated Electrons, Angew. Chem. Int. Ed., 2014 (available online Jul 14)
- Robert J Hamers, Jason Bandy, Di Zhu, Photoemission from diamond films and substrates into water: Dynamics of solvated electrons and implications for diamond photoelectrochemistry, Faraday Discussion, (accepted)
- Zhu Di, Liu Ran-ran, Li Hai-long, Chen Tao, Tian Wenyu, Sun Mao, Li Chunli, Hydrothermal Synthesis of Titania Powder with Different Particle Sizes, Acta Scientiarum Naturalium Unversitatis Pekinensis, 2010, 46(4): 525-530
- Robert J Hamers, Di Zhu, Photocatalytic Activation and Conversion of N2 and Other Small Molecules, under patent examining. (Selected as candidate for WARF Innovation Award)

Dr. Le Lu Power Environmental Energy Research Institute **EDUCATION**

- Ph.D, Petroleum Engineering, University of Southern California, Los Angeles, CA Sept 2015
- o Master of Engineering, Hydrogeology, Nanjing University, Nanjing, China, Dec 2008
- Bachelor of Science, Hydrogeology, Nanjing University, Nanjing, China July 2005

EXPERIENCE

- o Research Scientist, Power Environmental Energy Research Institute, 2014-present
- o Post-doc Researcher, University of Southern California 2014
- o Graduate Teaching Assistant, University of Southern California 2012 2014
- o Graduate Research Assistant, University of Southern California 2009 2014
- Research Assistant, Nanjing University 2006 2009

SELECTED PUBLICATIONS

- 1. **Lu, L.** and Zhang, D. 2015. Assisted history matching for fractured reservoirs by use of Hough-transform-based parameterization. SPE Journal 20(5), 942-961.
- 2. Wu, J.C., **Lu**, **L.**, and Tang, T. 2011. Bayesian analysis for uncertainty and risk in a groundwater numerical model's predictions. Human and Ecological Risk Assessment: An International Journal 17(6), 1310-1331.
- 3. Wu, J.C., **Lu**, **L**. 2010. Uncertainty analysis for groundwater modeling. Journal of Nanjing University (Natural Sciences) 47(3), 227-234.
- 4. **Lu, L**. and Wu, J.C. 2010. Bayesian analysis of uncertainties in groundwater numerical simulation. Journal of Hydraulic Engineering 41(3), 264-271.
- 5. **Lu, L.** and Wu, J.C. 2009. Bayesian method for groundwater uncertainty analysis using pumping test data. The 7th International Conference on Calibration and Reliability in Groundwater Modeling, Wuhan, China, Sept. 20-23, 2009.
- 6. **Lu, L**., Wu, J.C., and Chen, J.Y. 2008. Identification of hydrogeological parameters based on the Bayesian method. Hydrogeology and Engineering Geology 35(5), 58-63.
- Lu, L., Wu, J.C., and Wang, J.J. 2008. Monte Carlo modeling of solute transport in a porous medium with multi-scale heterogeneity. Advances in Water Sciences 19(3), 34-39.

PROFESSIONAL ACTIVITIES

- Invited Seminar Speaker, Department of Civil and Environmental Engineering, Stanford University. December 8, 2015.
- Invited Seminar Speaker, as part of the graduate course: Well completion, stimulation, and damage control, Department of Chemical Engineering and Materials Science, University of Southern California, July 23, 2015.

SKILLs

- Assisted history matching techniques: Ensemble Kalman filter, Ensemble smoother, Bayesian methods
- Uncertainty quantification techniques: Probabilistic collocation method, moment equation approaches,
- o Bayesian methods, Monte Carlo
- Programming languages: Fortran, C/C++, Matlab
- o Reservoir modeling software: ECLIPSE, MODFLOW, MT3D, SGeMS, GSLIB

6. Budget

YEAR 1 PROPOSAL BUDGET							
PROPOSING INSTITUTION/ORGANIZATION							
California Institute of Technology							
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR							
William A. Goddard, III							
A. KEY PERSONNEL: PI/PD, Co-PIs, Faculty and Other Senior Associa	ates		CPG-Funded	1		Funds	Funds
List each separately with name and title. (A.7. Show number in bra	ckets)		Person-month	S		Requested By	Granted by CPG
	CAL		ACAD	SUMR		Proposer	(If Different)
1. William A. Goddard, III - PI	1.20					20,90	09 \$
2. Andres Jaramillo-Botero - Senior Scientist	12.00					111,3	83
3.							
4.							
5.							
6. () OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION	PAGE)						
7. (2) TOTAL KEY PERSONNEL (1-6)	13.20					132,2	92
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)							
1. () POSTDOCTORAL ASSOCIATES							
2. () OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER,	ETC.)						
3. () GRADUATE STUDENTS							
4. () UNDERGRADUATE STUDENTS							
5. () SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)							
6. (1) OTHER - Computer Technician						2,50	00
TOTAL SALARIES AND WAGES (A + B)							92
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)							90
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)		\ \				173,8	82
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITER	M EXCEEDING \$5,000	.)					
Computer Equipment - 944,945							
						14 0	13
					τραιιά)	44,5	+3
2 EQREIGN					ind (Ell) (y	30.00	20
	and Training as of a	mulaianad in 4	ha				
F. PARTICIPANT SUPPORT (for meetings, symposia, conferences	and Training costs e	nvisionea in t	ne proposal tol	NON-employ	ees)		
1. STIPENDS \$							
2. IRAVEL							
4. OTHER							
	TOTAL PAR	TICIPANT CO	515				
						0.7/	~~
1. MATERIALS AND SUPPLIES						3,70	00
3. CONSULTANT SERVICES						50	50
4 COMPLITER SERVICES							
5. SUBAWARDS - PEER Institute						350.0	00
6. OTHER						000,0	
TOTAL OTHER DIRECT COSTS						354.2	63
H. TOTAL DIRECT COSTS (A THROUGH G)						603.0	88
I. INDIRECT COSTS (F&A) (SPECIFY RATE AND BASE)						,-	
Modified Total Direct Costs (64.3%)							
TOTAL INDIRECT COSTS (F&A)						149,9	12
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)						753,0	00
K. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)						753,0	00 \$
L. COST SHARING: PROPOSED LEVEL	GREED LEVEL IF DIF	FERENT: \$	_				.
PI/PD TYPED NAME AND SIGNATURE*	DATE				FOR	CPG USE ONLY	
				F	BUDGET REVI	EW AGAINST GUIDELI	INES
ORG. REP. TYPED NAME & SIGNATURE*	DATE		Date C	Checked	ľ	SSUES Y/N	INITIALS

YEAR 2 PROPOSAL BUDGET						
PROPOSING INSTITUTION/ORGANIZATION						
California Institute of Technology						
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR						
William A. Goddard, III						
A. KEY PERSONNEL: PI/PD, Co-PIs, Faculty and Other Senior Associates	6		CPG-Funded		Funds	Funds
List each separately with name and title. (A.7. Show number in bracke	ts)	F	Person-months		Requested By	Granted by CPG
	CAL	AC	AD SUM	R	Proposer	(If Different)
1. William A. Goddard, III - PI	1.20				21,536	3
2. Andres Jaramillo-Botero - Senior Scientist	12.00				114,725	
3.						
4.						
5.						
6. () OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PA	AGE)					
7. (2) TOTAL KEY PERSONNEL (1-6)	13.20				136,261	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)						
1. () POSTDOCTORAL ASSOCIATES						
2. () OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ET	C.)					
3. () GRADUATE STUDENTS						
4. () UNDERGRADUATE STUDENTS						
5. () SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)						
6. (1) OTHER - Computer Technician					2,500	
TOTAL SALARIES AND WAGES (A + B)					138,761	
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)					40,241	
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)					179,002	
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM E	XCEEDING \$5,000.	.)				
TOTAL EQUIPMENT						
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSE	SSIONS OR WITH	IN-EU OR WITHI	N CHINA OR WITH	IIN AUSTRALIA)		
2. FOREIGN					30,000	
F. PARTICIPANT SUPPORT (for Meetings, Symposia, Conferences and	nd Training costs e	nvisioned in the	proposal for NON	employees)		
1. STIPENDS \$						
2. TRAVEL						
3. SUBSISTENCE						
4. OTHER						
TOTAL NUMBER OF PARTICIPANTS ()	TOTAL PAR	TICIPANT COST	3			
G. OTHER DIRECT COSTS						
1. MATERIALS AND SUPPLIES					9,109	
2. PUBLICATION/DOCUMENTATION/DISSEMINATION					1,000	
3. CONSULTANT SERVICES						
4. COMPUTER SERVICES						
5. SUBAWARDS - PEER Institute					350,000	
6. OTHER						
TOTAL OTHER DIRECT COSTS					360,109	
H. TOTAL DIRECT COSTS (A THROUGH G)					569,111	
I. INDIRECT COSTS (F&A) (SPECIFY RATE AND BASE)						
Modified Total Direct Costs (64.3%)						
TOTAL INDIRECT COSTS (F&A)					140,889	
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)					710,000	
K. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)					710,000 \$	6
L. COST SHARING: PROPOSED LEVEL AGF	REED LEVEL IF DIF	FERENT: \$				
PI/PD TYPED NAME AND SIGNATURE*	E			FO	R CPG USE ONLY	
				BUDGET REV	IEW AGAINST GUIDELINES	
ORG. REP. TYPED NAME & SIGNATURE* DAT	E		Date Checke	d	ISSUES Y/N	INITIALS

PROPOSING INSTITUTION/ORGANIZATION						
California Institute of Technology						
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR						
William A. Goddard, III						
A. KEY PERSONNEL: PI/PD, Co-PIs, Faculty and Other Senior Associa	ates		CPG-Funded		Funds	Funds
List each separately with name and title. (A.7. Show number in brack	ckets)	1	Person-month	s	Requested By	Granted by CPG
	CAL	AC	AD	SUMR	Proposer	(If Different)
1. William A. Goddard, III - PI	1.20				22,182	\$
2. Andres Jaramillo-Botero - Senior Scientist	12.00				118,166	;
3.						1
4.						
5.						
6. () OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION	PAGE)					
7. (2) TOTAL KEY PERSONNEL (1-6)	13.20				140,348	3
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)				1		*
1. () POSTDOCTORAL ASSOCIATES						
2. () OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, I	ETC.)					
3. () GRADUATE STUDENTS				-		
4. () UNDERGRADUATE STUDENTS						
5. () SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)						
6. (1) OTHER - Computer Technician					2,500	
TOTAL SALARIES AND WAGES (A + B)	142,848	1				
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)	41,426					
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)					184,274	<i>i</i>
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM	A EXCEEDING \$5,000.)					
TOTAL EQUIPMENT						
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POS	SESSIONS OR WITHIN	I-EU OR WITH	IN CHINA OR	WITHIN AUSTRALIA)		
2. FOREIGN					30,000	
F. PARTICIPANT SUPPORT (for Meetings, Symposia, Conferences	and Training costs en	visioned in the	proposal for	NON-employees)		
1. STIPENDS \$						
2. TRAVEL						
3. SUBSISTENCE						
4. OTHER						
TOTAL NUMBER OF PARTICIPANTS ()	TOTAL PART	ICIPANT COST	S			
G. OTHER DIRECT COSTS						
1. MATERIALS AND SUPPLIES					6,881	
2. PUBLICATION/DOCUMENTATION/DISSEMINATION					1,000	
3. CONSULTANT SERVICES						
4. COMPUTER SERVICES						
5. SUBAWARDS - PEER Institute					350,000	
6. OTHER						
TOTAL OTHER DIRECT COSTS					357,881	
H. TOTAL DIRECT COSTS (A THROUGH G)					572,155	
I. INDIRECT COSTS (F&A) (SPECIFY RATE AND BASE)						
Modified Total Direct Costs (64.3%)						
					4.40.045	. T
					142,845	
					/15,000	
					715,000	Φ
	ATE	LIVENII: \$				
				PLIDGET	REVIEW AGAINST CHIDELINE	-8
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TOTAL 3 YEARS PROPOSAL BUDG	FT						
PROPOSING INSTITUTION/ORGANIZATION							
California Institute of Technology							
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR							
William A. Goddard, III							
A. KEY PERSONNEL: PI/PD, Co-PIs, Faculty and Other Senior Associa	ates		CPG-Funded			Funds	Funds
List each separately with name and title. (A.7. Show number in brack	ckets)		Person-month	S		Requested By	Granted by CPG
	CAL	A	CAD	SUMR		Proposer	(If Different)
1. William A. Goddard, III - PI	1.20					. 64,627	\$
2. Andres Jaramillo-Botero - Senior Scientist	12.00					344,274	
3.							
4.							
5.							
6. () OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION	PAGE)						
7. (2) TOTAL KEY PERSONNEL (1-6)	13.20					408,901	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)							
1. () POSTDOCTORAL ASSOCIATES							
2. () OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER,	ETC.)						
3. () GRADUATE STUDENTS							
4. () UNDERGRADUATE STUDENTS							
5. () SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)							
6. (1) OTHER - Computer Technician						7,500	
TOTAL SALARIES AND WAGES (A + B)		416,401					
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)	120,756						
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)						537,157	
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEI	M EXCEEDING \$5,000	.)					
Computer Equipment - \$44,943							
							r
						44,943	
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POS	SSESSIONS OR WITH	IN-EU OR WITH	HIN CHINA OR	WITHIN AUSTRA	ALIA)	00.000	
2. FOREIGN						90,000	
F. PARTICIPANT SUPPORT (for Meetings, Symposia, Conferences	and Training costs e	nvisioned in th	e proposal for	NON-employees	;)		
1. STIPENDS \$							
2. TRAVEL							
3. SUBSISTENCE							
4. OTHER							
TOTAL NUMBER OF PARTICIPANTS ()	TOTAL PAR	TICIPANT COS	TS				
G. OTHER DIRECT COSTS							
1. MATERIALS AND SUPPLIES						19,753	
2. PUBLICATION/DOCUMENTATION/DISSEMINATION						2,500	
3. CONSULTANT SERVICES							
4. COMPUTER SERVICES						4 050 000	
5. SUBAWARDS - PEER Institute						1,050,000	
6. OTHER						4 070 050	
						1,072,253	
						1,744,334	
Modified Total Direct Costs (64.3%)							
TOTAL INDIRECT COSTS (F&A)						433.646	
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)						2.178 000	
K. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)						2,178,000	\$
L. COST SHARING: PROPOSED LEVEL	GREED LEVEL IF DIF	FERENT: \$				_,,	Ŧ
PI/PD TYPED NAME AND SIGNATURE*	DATE	·			FOR	CPG USE ONLY	
				BUD	DGET REV	EW AGAINST GUIDELINE	S
ORG. REP. TYPED NAME & SIGNATURE*	DATE		Date C	hecked	l	SSUES Y/N	INITIALS

KFUPM

The College of Petroleum Engineering and Geosciences (CPG) Partnership Proposal PI: Professor William A. Goddard, III

Title: First-Principles Based Models, Methods and Experiments on Reversible Shear Thickening Fluids for Drilling, Stimulation, Conformance Control, and EOR Operations Budget Justification

Budget Justification

Senior Personnel: A portion (10% effort, 1.20 calendar months) of the salary and benefits of the Principal Investigator (PI) Professor William A. Goddard (**Caltech**) are being requested for his efforts in directing the Caltech part of this proposed research program.

Other Personnel: A portion (100% effort, 12 calendar months) of the salary and benefits of Senior Scientist Dr. Andres Jaramillo-Botero are being requested for his efforts in the daily oversight of this proposed research program.

Funds are requested for a Computer Technician (5% effort, 0.60 calendar months) to manage the Godddard computer systems to be used for this proposed research program.

Fringe Benefits: Fringe benefits are charged on senior personnel at 29%, but not on graduate or undergraduate students.

Travel: Funds are requested for foreign travel of Caltech personnel to meet with KFUPM (\$24,000) and attending international conferences (\$6,000). Typical estimated travel per person is as follows:

Purpose and	# of	# of	# of	Air	Lod-	Meals	Trans-	Reg	Total
Location	trips	days	travelers		ging		port		
Collaborative	1	5	1	4,000					\$4,000
Meetings w/									
KFUPM									
International	1	3	1	1,200	700	400	200	500	\$3,000
Res. Conf.									

KFUPM: Total trips/ yr. = 3; total travelers per trip = 2; $4,000 \times 3 \times 2 = 24,000$. Int'l Res. Conf.: Total trips/yr. = 1; total travelers per trip = 2 = $3,000 \times 2 \times 1 = 6,000$

Equipment: In year one, we will purchase four Dell R730 server nodes estimated at \$10,308 each plus 9% tax. Estimated total cost will be \$44,943.

Other Direct Costs:

Materials and Supplies: Budget allocates \$19,752 over three years to purchase various consumable supplies to be used in the project. This amount includes \$17,000 over three years in costs to maintain the hardware and software to be used in the project and in operating these resources.

Publication Costs: Budget allocates \$2,500 over 3 years for publication charges and dissemination of results through printed media.

Subcontract: Budget allocates \$350,000 per year for subcontract costs to PEER Institute.

Indirect Costs: Caltech's indirect cost rate is 64.3% of modified total direct costs, excluding subcontract amount above \$25,000.



738 Arrow Grand Circle, Covina, CA 91722, USA. Tel (626) 858-5077, Fax (626) 858-9250

POWER ENVIRONMENTAL ENERGY RESEARCH INSTITUTE

Budget Justification

Labor Cost

The estimated annual working hours of participated co-PI, senior scientists and junior scientists from PEERi and their base salary rates are:

Dr. Yongchun Tang (co-PI): Rate = \$96.15, Hours = 260, total \$25,000

Dr. Chengyang Jiang: Rate = \$48.08, Hours = 780, total \$37,500

Dr. Di Zhu: Rate = \$48.08, Hours = 780, total \$37,500

Dr. Le Lu: Rate = \$40.86, Hours = 1040, total \$42,500

Technician: Rate = \$26.44, Hours = 2080, total \$55,000

Clerical: Rete = \$21.63, Hours = 693, total \$15,000

The total annual salary from PEERi is \$212,500

The total annual fringe benefit is \$42,500 (based on the 20% rate, which is from our current practice).

Materials and Supplies

The materials cost of **\$60,000 each year** includes purchasing of chemical supplies, standard gas, mechanical parts, computer components and miscellaneous lab supplies. Purchasing activities will happen in a similar pattern during the there-year period. The estimation is based on previous experience.

Chemical for polymer synthesis and characterization: Unit price = \$350 x 100 units = \$35,000

Core samples for polymer performance tests: Unit price = 340×50 units = 17,000

Computer Components for basin modeling and history matching: Unit price = 200×10 units = \$2,000

Miscellaneous laboratory supplies and tools: Unit price = $60 \times 100 \text{ units} = 6,000$

Publication

Budget of **\$5,000 each year** is allocated to publish research result in peer-reviews journals through the project. The estimation is based on average publication cost at the market.

<u>Travel</u>

Domestic and international travels are expected to happen in a similar pattern for each budget period. The following table summarizes the estimated number of travels occurred every year.

Tuble if Estimated Hamber of Trips for Each Stager Ferror								
Purpose/Budget Period	Year 1	Year 2	Year 3					
Attending U.S. Research Conference	1	1	1					
Attending International Research Conference	1	1	1					
Visit KFUPM	3	3	3					

Table 4: Estimated Number of Trips for Each Budget Period

We expect to spend \$30,000 each year in travel, which include redeems for travels to attend research conferences and visit research partners in KFUPM. The co-PI, project manager and one senior scientist plan each to visit KFUPM once every year to collaborate with KFUPM colleagues on the research program. The estimated cost is \$5,000 per person per trip for one week stay. We also propose to attend one international research conference and one U.S. research conference each year. We will send three travelers each time. The cost for international research conference is 10,000 and for U.S is 5,000. The estimated travel cost includes registration fee, airfare, lodging, meal and local transportation. We shall plan our trips in advances and seek through local travelling agencies or Internet for the lowest possible prices.

<u>Equipment</u>

We have all the equipment needed for this project. We do not plan to purchase any major equipment.

Power Environmental Energy Research Institute

738 Arrow Grand Circle, Covina, CA 91722, USA. Tel (626) 858-5077, Fax (626) 858-9250

Professor William A. Goddard, III Director, Materials and Process Simulation Center California Institute of Technology

RE: Joint Proposal to the King Fahd University of Petroleum & Minerals (KFUPM)

Dear Professor Goddard:

Power Environmental Energy Research Institute (PEERi) has a general vision on conducting on-going and systematical R&D programs on the way to improve our fuel economics and environmental preservation, utilizing novel materials and chemical process designs, in particular the innovative nano-scale polymeric products for improved hydrocarbon recovery. We are pleased to collaborate with Caltech in this 5-year proposal to the King Fahd University of Petroleum & Minerals (KFUPM), entitled "FIRST-PRINCIPLES BASED MODELS, METHODS AND EXPERIMENTS ON REVERSIBLE SHEAR THICKENING FLUIDS FOR DRILLING, STIMULATION, CONFORMANCE CONTROL, AND EOR OPERATIONS" to integrate modern computational simulation programs and advanced synthetic chemistry for "smart" polymers for oilfield applications. Previously functioning as an off-campus laboratory from 2000 to 2009, the PEERi has extensive project development and management experiences, especially in the novel materials and chemical synthesis and evaluation. We believe that development of "smart" polymers that would self-adaptive to the reservoir conditions has the potential for significant process improvements and energy cost saving in hydrocarbon fuel productions. Additionally, "smart" polymers offer several technical and environmental advantages when being used in drilling, cementing, stimulation, conformance controlling, and enhanced oil recovery operations. This proposal focuses on an integrated theoretical and experimental studies on fundamental science of the "smart" polymers. PEERi has extensive experience in chemical synthesis and laboratorial evaluation of special materials and process optimization, and can provide important additions to Caltech on the novel material design of the research.

PFFR

PEERi will assemble a strong research team composing expertise in Organic Chemistry, Physical Chemistry, Chemical Engineering, and Petroleum Engineering aspects to conduct all proposed R&D studies. PEERi is providing an in-kind cost-sharing of \$150,000 every year to the proposed sub-awarding contract of total \$500,000, contingents to the eventual funding of the project of from KFUPM. The net request budget will be \$350,000 each year for 3 years. We believe this research study has significant potentials for success that could benefit both Caltech and PEERi, as well as KFUPM.

If you have any questions, please feel free to contact me at (626) 685-4539 (cell) or email me at tang@peeri.org.

Yongchun Tang Power Environmental Energy Research Institute 738 Arrow Grand Circle Covina, CA 91722 (626) 858 – 5077 (office)

7. Intellectual Property Plan

Intellectual property arrangements will be based on Caltech's technology transfer work experience in sponsored-research projects where Caltech successfully created and implemented partnership agreements that merge industry, university, and national laboratory efforts in proper compliance with funding agencies, local or foreign. Researchers in this effort will present patentable information in monthly meetings, and the originating institutions will file invention disclosures once ownership is agreed upon. Publication drafts will be circulated and discussed in task teams before submission. The parties agree that the selected parties shall jointly own inventions made jointly by selected parties' members.

A commercialization partner will be required in case there's a need to transition the technology to the research, industrial, and operational communities. The team members believe that the appropriate time to engage a commercialization partner will be after the conclusion of the proposed 3-year work. If such need arise, Saudi Aramco, would be given first rights to licensing, or else if deemed appropriate, we would begin the process of identifying a different commercialization partner midway through this project, and actually begin contract negotiations as soon as possible after the 3rd year of this work is concluded. The process of identifying a commercialization partner will begin with identification of partner selection criteria that will consider both the anticipated technology readiness level (TRL) at the conclusion of year 3 and the resource requirements of a partner such as funding, staff capabilities, equipment and appropriate technical experience. We will evaluate interested parties against the selection criteria. We believe this process will result in the selection of one or more partners with a high likelihood of commercial success.

8. References

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9. Current and Pending Support

Current and Pending Project and Proposal Submissions

Principal Investigator: William A. Goddard, III

Title	Source	Period of Performance	Effort	Annual \$
Current Support				
Joint Center of Artificial Photosynthesis (JCAP II)	DOE DE-SC0004993	9/30/2015 - 9/29/2020	0.24 Cal	464,569
Brain Receptor E Coli Kl	NIH R01AI040567	7/1/2011 - 6/30/2016	0.12 Cal	38,330
Metal Oxice Functionalization of Alkanes	CHE-1214158	6/1/2015 - 5/31/2016 Should be 3 years	0.12 Cal	130,000
Metastable Solids: Pressure + Shear	DARPA W31P4Q13-1-0010	1/14/2013 - 7/15/2016	0.24 Cal	100,000
Mulitscale Modeling Novel Energetic Insensitive Materials	ONR N00014-16-1-2059	12/1/2015 - 11/30/2018	0.36 Cal	150,000
Multiscale Modeling of Synthetic High Hardness Ductile Alloys	DOD-DARPA W31P4Q13-1-0001	4/20/2015 - 1/20/2016	1.00 Cal	105,000
B4C (Rutgers)				
Multiscale Modeling and Design of Materials for Extreme	ARL W911NF-11-R-00001	1/1/2012 - 12/31/2016	0.69 Cal	114,839
Dynamic Environments (Johns Hopkins Univ. Subcontract)				
EFRI-ODISSEI: DNA Nanostructures	NSF EFRI-1332411	8/1/2013 - 7/31/2017	0.12 Cal	173,301
Low Temperature growth GaN Films	DARPA HR0011-14-2-0003	9/1/2013 - 10/17/2016	0.60 Cal	150,065
DMREF: Novel BCN Systems	NSF DMR-1436985	9/1/2014 - 9/30/2017	0.24 Cal	111,111
3D Structures Sweet & Bitter Taste Receptors (Phase 1 & 2)	Cargill Incorporated	4/1/2014 - 3/31/2017	0.60 Cal	150,000
Design Materials High-Energy Electrochmical Devices	Bosch BERN 2015 07.23.CS.15	8/1/2015 - 7/31/2017	0.36 Cal	150,000
Computational Materials Science Center (PI: USC)	DE-SC0014607	9/15/2015 - 9/14/2016	0.36 Cal	165,000
Nanoporous Pt – Catalysts	NSF CBET 1512759	6/17/2015 - 8/31/2018	0.36 Cal	114,726
Synergistic Modulation of Pain Signals	GIST 2015	1/1/2016 - 12/31/2016	0.12	45,000
Pending Support				
DMREF: Collaborative Proposal: Computationally Guided	15-608	Submitted 1/19/2016 (4 years)	0.48 Cal	147,500
Design of Advanced Electrochemical Devices	15-000			
Brain Endothelial Cell Receptor for Escherichia Coli	Renewal of 2R01 AI040567-16A1	Submitted 2/12/2016 (5 years)	0.12 Cal	30,000
Development of Advanced Computational Models and Methods	DE-FOA-0001384	Submitted 3/31/2016 (5 years)	0.36 Cal	143,925
in Application to Advanced Polymer and Iorganic Electrolytes	AOI-8			
Massachusetts-California Center for Non-equilibrium and Meso-	DE-FOA-0001528	Submitted 4/25/2016 (4 years)	0.6 Cal	250,000
Scale Properties of Functional Materials				

CURRENT SUPPORT (Andres Jaramillo-Botero)

	· · · ·		Period of		Total Award
Source	Title	Grant No.	Performance	Effort	Amount
NSF	Metal Oxide Functionalization	CHE-1214158	6/1/2012 -	1	\$390,000
	of Alkanes		5/31/2016		
DARPA ARO	Metastable Solids: Pressure +	W31P4Q13-1-0010	1/14/2013 -	1	\$1,682,000
	Shear		7/15/2017		
DOE	Computational Synthesis of	USC Sub (68192992);	9/15/2015 -	3	\$165,000
	Materials Software Project	DOE Main (DE-	9/14/2016		
		SC0014607)			
ONR	Novel Energetic but Insensitive	N00014-16-1-2059	12/1/2015 –	3	\$450,000
	Materials		11/30/2018		
ARL	Multiscale Modeling and Design	W911NF-11-R-00001	1/1/2016 -	2	\$114,839
	of Materials for Extreme		12/31/2016		
	Dynamic Environments (Johns				
	Hopkins Univ. Subcontract)				
DARPA	Low Temperature growth GaN	HR0011-14-2-0003	9/1/2013 -	1	\$814,975
	Films		10/17/2016		
NSF	DMREF: Novel BCN Systems	DMR-1436985	9/1/2014 -	1	\$333,333
			9/30/2017		

PENDING SUPPORT (Andres Jaramillo-Botero)

ONR MURI	Predicting and Measuring Physicochemical and Mechanical Processes in Dynamic Response of Solid Composites at Extreme Conditions	ONR-15-FOA-0011, Topic 21	12/7/2015 (5 years)	9.60	\$7,500,000
ONR MURI	Large-Scale Arrays of Addressable, Registered and Atomically Precise Graphene	ONR-15-FOA-0011, Topic 16	11/16/2015 (5 years)	2.40	\$959,750
ONR DURIP	The Energetic Materials ab Initio Reactive Molecular Dynamics and Kinetics Simulator	PA-AFRL-AFOSR- 2015-0001	9/25/2015 (1 year)	0.00 Equip only	\$294,990
DOE	Development of Advanced Computational Models and Methods in Application to Advanced Polymer and Inorganic Electrolytes	DE-FOA-0001384 AOI-8	3/31/2016 (5 yrs)	1.80	\$719,625
DOE Subcontract with Harvard University (PI Shankar)	Massachusetts-California Center for Non-equilibrium and Meso-Scale Properties of Functional Materials	DE-FOA-0001528	4/25/2016 (4 years)	3	\$1,000,000
DOE Subcontract with UCLA (PI Huang)	New Tools and Software Development with Experimental Validation for Multiparadigm Catalyst Design for Fuel Cells	DE-FOA-0001528	4/25/2016 (4 years)	9	\$1,600,000

Dr.	Yongchun	Tang
Dro	liact	

Project	Source	Efforts (month)		
		2016	2017	2018
Geochemical assessment of unconventional	Joint Industrial	2	2	2
resource, shale gas/oil	Project (JIP)			
Geochemical enhanced hydrocarbon production Joint Industrial			2	2
	Project (JIP)			
High-T drilling fluid loss control	Private Industry	1	1	1
Nano-suspension gelling cementing agents	Private Industry	1	1	1
Non-oxidative methane conversion	US-DOE	2	1	0
Reverse Osmosis water-treatment	Private Industry	1	1	1
"Smart" polymer fluid development (Pending)	KFUPM	1.5	1.5	1.5

Dr. Raymond Jiang

Project	Source	Efforts (month)		
		2016	2017	2018
High-T drilling fluid loss control	Private Industry	2	1	0
Nano-suspension gelling cementing agents	Private Industry	1	1	1
Reverse Osmosis water-treatment	Private Industry	2	1	2
"Smart" polymer fluid development (Pending)	KFUPM	4.5	4.5	4.5

Dr. Di Zhu Droject

Project	Source	Efforts (month)		
		2016	2017	2018
Geochemical enhanced hydrocarbon production	Joint Industrial Project (JIP)	2	4	3
Non-oxidative methane conversion	DOE	3	3	0
"Smart" polymer fluid development (Pending)	KFUPM	4.5	4.5	4.5

Dr. Le Lu Project Source Efforts (month) 2016 2017 2018 Geochemical enhanced hydrocarbon Joint Industrial 4 4 2 production Project (JIP) Nano-suspension gelling cementing agents Private Industry 1 1 1 "Smart" polymer fluid development (Pending) KFUPM 6 6 6

10. Supplementary Material

Experimental programs to be conducted in PEERi will focus on the molecular design, synthesis and screening of the "smart" polymer fluid; and to explore and evaluate the cost-effective and environmentally friendly oilfield application feasibility for EOR/IOR. The laboratory methods and designs of experiment include:

Characterization of "smart" polymers

Through years of intensive studies, numbers of special polymers have been made, and many of them are now commercially available. Therefore, the objective of this work is to demonstrate that there exist certain types of special polymers that can be used as "smart" polymers when added in the aqueous solution, which are suitable for the oilfield applications. From our previous studies at PEERi, we have identified at least two of such candidates that display distinct self-adaptive thickening behaviors respectively. In this program, we shall further examine these candidates, with a focus to improve our basic understandings of the physical/chemical process of polymer self-thickening and adaptiveness in possible field operations. For the laboratory screening purposes, a number of "smart" polymers dissolved in the synthetic brines consisting of various salinity, hardness and pH will be used.

Couettee rheometer response

As "smart" polymer fluids are injected into a reservoir, the shear rate, which is related to flow velocity will change substantially from near wellbore regions to in-depth reservoirs, as well as from high permeability zones to low permeability zones. In this study, the rheological properties of candidate "smart" fluids will be systematically tested within the range of shear stress experienced undergrounds ($0.1 \sim 200 \text{ s}^{-1}$). Also, we will comprehensively analyze the effects of concentration, temperature (from room to temperature up to 85 °C), and water salinity on the "smart" polymer rheology, A couple of advanced Anton Paar MCR 302 Rheometer will be heavily used to measure the rheological properties of "smart" polymer fluids, such as G' (elastic behavior) and G" (viscous behavior), etc.



Figure 3 Response curves of the "smart" polymer fluid and the regular hydrolyzed polyacrylamide (HPAM) in 2% NaCl showing shear thickening behavior with different viscosity V1 and V2.

Core flood tests and routine analysis

Flow behavior in porous media

Rheological properties of "smart" polymer fluids measured by conventional rheological instruments that produce pure shear flow need to be calibrated to predict the pressure-to-flow relationship in porous media. In this study, we will design a series of core-flow tests to study the flow behavior of "smart" fluids in porous media. The flow resistance effects will be determined by calculating an apparent viscosity based on the recorded value of the flow rate and pressure difference over the core. The effects of flow rate (0 ~ 30 ml/min) and rock permeability (200 ~ 2000 mD) on the apparent viscosity of "smart" fluids will be tested and analyzed. Also we will employ the residual resistance factor (RRF) to evaluate the polymerinduced permeability reduction (see Figure 3).

A known condition of an oilfield in middle-east will be selected as our parallel core flooding background (see Figure 4). The viscosity of the crude oil samples (30 ~ 100 cp) at typical

reservoir temperature conditions (40 ~ 85 °C). The synthetic brine solution with salinity ~ 5000 ppm NaCl equivalent will be used. In general, fluid in a brine water flooding operation acquires a high velocity in high-K (i.e., 2000 mD) zone compared to the low velocity in low-K (i.e., 2000 mD) zone. Accordingly we will design and manufacture a heterogeneous physical modelled core. One high-permeability core (2000 mD) will be placed in between two low-permeability cores (200 mD) in parallel to mimic the different flow channels in fields. To avoid the premature breakthrough, selective "smart" polymer solutions will be added to the injecting fluid. With the self-adaptive shear-thickening property of the "smart" polymer fluid, we expect to achieve the significant slowing-down of flow in the high-K zone than in the low-K zones. On the basis of the laboratory testing and analyses, a group of curves and data will be collected to as reliable input of typical parameters of the monomer selections of the "smart" polymer for molecular modeling and numerical simulations, such as the molecular weight of polymer, the fluid viscosity, polymer concentration, shear rate, and amount of polymer adsorbed on cores, etc.



Figure 4 Schematic diagram of the multi-core flooding experiment. **Numerical simulation and history matching**

To achieve a better understanding of the self-adaptive thickening that impacts the ultimate recovery, we will run limited number of experiments to validate the lab-scale reservoir and model, considering the limited availability of homogeneous core plugs of suitable size and permeability for core flooding experience. Instead, we will apply the numerical simulation and history matching methods to correlate the experimental data. The lab-scale reservoir simulation model will be capable of reproducing similar results demonstrate in the physical experiments. With this model, we will be able to run a large numbers of "digital-core" flooding studies. Consequently, the lab-scale model can be scaled up for the field-scale simulations to preliminary quantify the potential of the "smart" polymer fluids in EOR/IOR.

For the theoretical studies, we propose to use a hierarchical multiscale simulation strategy (see Figure 5) involving QM (XYGJ-OS and generalized dispersions for DFT), unreactive and reactive MM/MD simulation (UFF, Dreiding, ReaxFF, VBPQReax, aARRDyn), optimization (GARFfield) and analysis (2PT) methods to design, characterize, optimize and screen reversible shear-thickening (non-Newtonian) fluids based on different nanoparticles (structures) solvent combinations. We will use QM prepared data to optimize our force fields for high accuracy and improved transferability, when and where needed.



Figure 5 General multiscale, multiparadigm strategy (adapted from Larentzos et al, 2015).

Conventional MD simulations are usually limited to the study of fluid flows with a very low Revnolds number and hence to non-Newtonian behavior, since largescale instabilities are prevented because of the relatively small size of system models and the Reynolds number remains very low even at extremely high shear rates, which leads to a non-Newtonian rather than turbulent behavior. [13]

Nonetheless, the advent of peta and exascale computing has

enabled increasingly large molecular system descriptions with atomistic resolution capable of accurately capturing shear viscosity of fluids and gels, using our conventional Dreiding,[8] UFF force fields, and others,[14] as well as other non-equilibrium phenomena such as material interfacial instabilities,[15-17] using our reactive force fields, ReaxFF and VBPQReax. The study of such systems is beyond state-of-the-art NEMD methods using conventional force fields, even using petascale computing power, because current methods lack the full chemical description of reactive. Conventional inter-atomic potentials used in NEMD cannot describe bond breaking and formation processes at the heart of chemical reactions and complex rearrangements underlying phase-transitions.

Polymer gel system models and validation

The general strategy for building molecular structures of polymers, nanoparticles, gels and fluids will involve using molecular builder to construct the individual molecules and combine them into a system model unit cell. Each structure will be optimized to a minimum energy tolerance using Dreiding or UFF or the final target force field (e.g. VBPQReax or Reax), then equilibrated at target temperature and pressure (for polymers and gels we will use the scaled effective solvent method[18]), then solvated with water and counter ions (to a net neutral charge), and subsequently used to validate system properties against experimental data (see Figure 6).



Figure 6 Structure preparation and validation, from monomer, build trimer, compute the rotational isomeric states table, build an n-mer structure within periodic boundary conditions, solvate with water and counter ions, and validate using experimental data (e.g. radius of gyration, density, etc.) **ReaxFF, VBPQReax reactive force fields and hyperdynamics**

To study the solid-liquid interactions and overall nanofluid dynamics and electro-kinetics (e.g. charged interactions between solid-solid and solid-ions in liquid), as well as the effects of nanoparticles properties on reversible shear-thickening behavior, we propose to use the ReaxFF Reactive force field[5] and the new polarizable valence bond theory based reax VBPQReax. ReaxFF is now one of the most widely reactive force field methods in the world.

Important and relevant capabilities and characteristics of ReaxFF are: 1) the charges are allowed to change every time step as bonds are formed or broken and they operate between all atoms, not just non-bonded ones (since bonded atoms may become non-bonded and vice versa); 2) the vdw interactions are included between all atoms, not just non-bonded atoms (since bonded atoms may become non-bonded and vice versa). This allows the valence bonding interaction to be monotonic attractive since the vdW inner wall balances the bond attraction: 3) all valence interactions depend on the bond order and go to cero as the bonds are broken. We assume that the BO is a sigmoid-like function of distance, going to a constant for small R and to zero for large R. We also assume that the bond energy is related to the BO by a simple function that is linear for small R. The three constants describing this sigmoid and the additional ones describing BE-BO are determined to fit the bond dissociation and reaction pathways for a huge number of reactions. ReaxFF also includes bond angle terms, but the actual energy as a function of angle includes important contributions from our vdW term. Similarly ReaxFF allows torsion and inversion terms, all of which go to zero as the bonds dissociate; and 4) all parameters are obtained directly from QM. Thus whenever we obtain a result from ReaxFF that seems strange, we simplify the system to be sufficiently small for QM and do a test. ReaxFF will be used to perform nanoparticle plus solvent structure prediction, as well as to study nanoparticle diffusion, fluid flow electrokinetics, and local and global phase transitions during deformation regimes.

We are continuing to refine the ReaxFF functional forms, in order to reduce the number of parameters while enabling descriptions in which parameters change smoothly down and across the periodic table (as done with our previous generic but not reactive force fields UFF[4] and Dreiding[19]). We have recently combined it conceptually with the Polarizable QEg (PQEg) methodology[20, 21] and introduced Valence Bond theory concepts to produce a highly accurate polarizable version of the force field engine, called VBPQReax. The original ReaxFF uses the QEq[22] method, which finds the atomic charges using the electronegativity and idempotential of each atom and how they are related to ionization potential (IP) and electron affinity (EA) to minimize the total energy E of a system. Instead, the new VBPQReax electrostatics describes each atom as a charged core with a fixed charge and a variable shell charge, both modeled with a Gaussian charge distribution. To prevent the shell from drifting away from the nucleus, the shell is attached to the core with a 2nd and/or 4th order spring force. Charges evolve according to an equation of motion with damping. This method of solving the system of N linear equations scales as O(N) and thus scales well to large systems. With a proper choice of the damping constant, charges are kept, as expected, approximately constant during bond vibrations. VBPQReax will enable accurate predictions of dielectric properties during the dynamics of chemical reaction processes, as well as changes in local and global dipoles that may underline a shear-thickening behavior. A prototype of VBPQReax developed by the Goddard group has shown excellent description of reaction steps and polarization at reaction temperatures.[23] The new approach allows an accurate description of the local polarization needed for describing dielectric and magnetic properties. Furthermore, it includes descriptions for the van der Waals (London) dispersion interactions from our ReaxFF-ulg

approach[3], validated against the D3 technique from Grimme[24], which may play an important role at the particle-particle, particle-rock interface in the fracking fluid.

Adaptive accelerated ReaxFF reactive (aARRDyn) hyperdynamics

To enable the timescales required to describe structural-reorganizations during nonequilibrium and near-turbulent reactive flows, we propose to use the adaptive Accelerated ReaxFF Reactive Dynamics (aARRDyn).[25] aARRDyn utilized the bond order concept in ReaxFF to identify bonds that can be boosted, allowing the reaction rates to be increased without affecting the proper reaction kinetics. Studies using aARRDyn have been successful at simulating reaction processes up to 5 minutes of reactive dynamics, and demonstrated for nucleation and growth of crystalline diamond thin films at low-temperatures[26]! aARRDyn is based on the adaptive boost potential introduced by Markwick et al[27] for conventional nonreactive MD. As opposed to the original formulation in which the boost criterion is bond length, in aARRDyn the boost a criterion is a function of bond orders that enable distinguishing bonded atoms from nearest neighbor atoms. Furthermore, the radical reactions are selectively avoided for acceleration, since these do not have any energy barrier (i.e. TST theory does not hold). When a radical is identified by ReaxFF under/over coordination terms, acceleration is turned off, until all radicals are consumed. aARRDyn will be used to explore long-term electrokinetic processes involved flow of a solvent through dynamically changing solid nanoparticle arrangements, as well as surface and interfacial re-arrangements near the rock formations.

Coupling to large-scale coarse-grain models in NPD

Current coarse-grain molecular dynamics (MD) approaches are not adequate to determine properties other than static (equilibrium) properties of polymer systems, due to the loss of molecular degrees-of-freedom during coarse graining. In polymer gel systems, we need to capture structural rearrangements, mechanical deformation, solvent interactions and changes in chemical reactivity while enabling accurate large-scale, long-term dynamics. One approach is to find appropriate scaling factors for the free energy of the system as a function of temperature and pressure. Our approach will be to incorporate explicit force terms to compensate for the missing degrees of freedom (e.g. shearing or squeezing of coarse-grain particles) within a dissipative particle dynamics (DPD) framework tuned to atomistic VBPQReax/ReaxFF simulations (hierarchy shown in Figure 5. The base conservative CG model for the polymer is obtained by computing interatomic distributions between the atomistic CG constituents (e.g. polymer dimer or trimer molecules), and the total interaction force includes pairwise additive dissipative and random forces acting on each particle. Repulsion strength between mesoparticles to describe the maximum repulsion between interacting particles will be obtained from atomistic force field, with weight functions to partition the conservative, dissipative and random forces. Español and Warren[28] showed that the dissipative force and the random force must satisfy a specific relationship for the system to have statistical mechanics behavior corresponding to the canonical ensemble, with a temperature associated to the relative amplitudes of the interactions. We use the Groot-Warren-velocity Verlet algorithm[29] to integrate the equations of motion. To couple VBPQReax/ReaxFF to DPD, we first perform simulations of molecular fragments at the VBPQReax/ReaxFF level while retaining all atomistic details to derive the DPD parameters, then we use these results as input to a coarse-grain DPD simulation. To estimate the DPD parameters we will calculate the solubility parameters of each CG component. First, for the system containing molecules of the same species, we will obtain the non-bonded energy of the model VBPQReax/ReaxFF atomistic MD simulations. Then each molecule is extracted to vacuum to calculate the non-bonded energy for the individual molecule. Thus, will provide the cohesive energy densities of the components at the experimental temperature. The DPD interaction parameters between different components will then be estimated from ReaxPQ MD simulations.

Energy conservation is guaranteed by adding an implicit internal energy and temperature for each coarse-grain particle, thereby allowing particles to exchange momentum and heat.[30, 31] From Maillet et al and Stoltz[32, 33] we expect to add reactions into the DPD while conserving energy by defining an additional CG particle variable associated with the extent of a reaction (i.e. reactions occur within CG particle and NOT through bond breaking between particles), which in turn requires input of reaction mechanisms and kinetics from VBPQReax/ReaxFF RMD. The chemical energy released/gained is translated to internal and kinetic energy. The resulting CG particle reactor model is deduced from the endothermic and exothermic reactions obtained via thermal decomposition simulations using VBPQReax/ReaxFF for each CG constituent and fitted to an Arrhenius form. The changes in chemical character are thereby expressed as changes to the inter-particle internal/external potential. Therefore, the variance of the particle internal energy includes a contribution corresponding to the energy associated with changes in chemistry. This uniquely incorporates explicit reaction dynamics via a reaction rate model calibrated from VBPQReax/ReaxFF.

We will use the DPD coarse-grain models to study the transition to turbulent flows from the nano-fluid under stress, and to study extensive (size-dependent) properties, such as mass transfer.

The 2-phase thermodynamics method (2PT)

Tracking the free energies and entropies will be essential to extract the rate dependent properties during static and dynamic shearing of the relatively large-scale heterogeneous systems of interest. To this end, we will use our two-phase thermodynamics (2PT) methodology (described below) from short (20ps) reactive MD trajectories [13-15]. The 2PT approach allows consistent partial calculation of free energies and entropies for each molecular or surface species in the system [73].





To obtain free energy and entropy from MD trajectories we use the Wiener-Khintchine theorem[9, 35] to obtain the spectral density from the Fourier transform of the velocity autocorrelation function. This density of states, DoS(v), can be used to derive the partition function and hence the standard thermodynamic properties. To avoid singularities in the thermodynamic properties we use a two phase model in which computed DoS(v) is partitioned into a solid phase form for which S(v) goes to zero smoothly at zero frequency (describing the vibrational density of states of a solid) and the DoS(v) for a gas of hard spheres. The gas phase component can be characterized with two parameters extracted from the MD trajectory: S(0) (which is proportional to the diffusion coefficient) and Ng, the total number of gas phase modes. The thermodynamics of the gas component is obtained from hard sphere theory based on these

two parameters. 2PT has now been applied to a number of systems with excellent results, including the thermodynamic and mechanical properties that lead to high-strength polymerbased double network hydrogels[36], accurately calculating the standard molar entropies and heat capacities of common liquids[37], and following the thermodynamics of a the rearrangement of the DNA three-way junction (involving ~50,000 atoms) [38]. The 2PT approach has the virtue that the free energies and entropies are attributed to each molecular or surface species in such a way that the sum over all entities adds up to the total. This allows the special regions dominating the change in entropy or free energy to be identified. In this project, we propose to use 2PT as a tool for understanding the changes in surface thermodynamics (e.g. entropy and free-energy) of reactions on nanoporous materials.

2PT will be used here to understand and benchmark the thermodynamics properties during equilibrium and non-equilibrium fluid flow, as a function of the solid and liquid phases.

Systematic first-principles based parameter optimization (GARFfield)

A critical component in our first-principles based design of reactive force fields is the fact that all parameters are trained from quantum data sets within a systematic optimization framework, the GARFfield force field optimization framework.[11] GARFfield uses a hybrid evolutionary and gradient based scheme to enable systematic multi-objective Pareto-optimal optimization of the force field parameters using QM prepared training datasets, hence improving accuracy and transferability over a wider range of compositions, interactions, and environmental conditions unexplored by experiments. GARFfield optimization objectives include charges, cell stress, stress-strain curves, geometries, lattice parameters, heats of formation, equations of state, and other energy based objectives. We propose to systematically re-optimize the VBPQReax force field parameters using QM data sets prepared specifically to account for potentially un-trained interactions between the nanoparticles and the solvent via the hybrid evolutionary and gradientbased multi-objective force field optimization framework, GARFfield.[11] GARField is available as an open source code for academic and research institutions from http://www.wag.caltech.edu/home/ajaramil/GARFfield.html. GARFfield will be used to systematically optimize ReaxFF/VBPQreaxFF for all the expected interactions in the nanofluids proposed under this effort.

NEMD shear simulation protocol

Simulations will be carried out for different densities, ranging from 0.5 to 0.84, temperatures from 0.75 to 1.5 (these state points are typical of the liquid state), and a particle size range to be determined. For each state point investigated, we will equilibrate the simulation box in the absence of shear and generate an equilibrium configuration. A shear rate $\dot{\gamma}$ will then applied by superimposing a linear velocity profile to match the shear rate, on the equilibrium velocities of all particles. We will then solve the Newtonian equations of motion using an NVT ensemble (constant number of particles, constant volume and controlled temperature) until a steady state is reached, at which point averages of properties of interest will be collected. The system will thus relax to its own steady-state flow profile, consistently with the periodic-boundary conditions. The SLLOD equations of motion, originally proposed by Hoover and Ladd[39], and proven to be equivalent to Newton's equations of motion for shear flow by Evans and Morriss[39] will then be applied. Though the temperature will be kept fixed using an explicit thermostat, the velocity fluctuations will not be constrained to remain the same far from equilibrium since particles will exert a drag on each other and secondary flow profiles will develop in the non-Newtonian regime.[40] Constraining the velocities fluctuations to remain the same leads inevitably to the formation of lanes for high enough shear rates[41] and to the alignment of particles into strings along the flow direction.[42] Reorganization of particles within the strings results in nonmonotonic variations of the shear viscosity with the applied shear, a phenomenon, which is

sometimes incorrectly (in the sense that it does not correspond to what takes place in colloidal suspensions) interpreted as an indication of shear thickening.[13, 42] From a practical point of view, avoiding constraints on the mechanical noise is achieved in this work by using a configurational (i.e. temperature is estimated only from spatial derivatives of the interaction energy) thermostat[42] to account for the dissipation of heat without affecting the steady-state flow profile. In essence, the solvent provides a heat bath for the colloidal particles and acts like a thermostat. In simulations where heat is removed through thermostatted shearing walls, a small increase in the applied shear rate gives rise to a large increase in temperature and in turn in pressure and viscosity[43], which should not be interpreted as shear thickening since the it is only due to the steep isochoric increase in temperature while the fluid remains well within the Newtonian regime.[13] We will use explicit solvent in our simulations, in order to capture its effect on the rheological behavior of the suspension.

We will test two shear viscosity algorithms, namely a direct perturbation of the nanofluid's unit cell (triclinic definition) and a reverse perturbation.[44] The former involves exchanging momenta between two particles in different regions of the simulation box every N steps to induce a shear velocity profile in the system, which enables a viscosity of the fluid to be calculated. This algorithm is corresponds to a reverse non-equilibrium MD approach to computing viscosity because the usual NEMD approach imposes a shear velocity profile on the system and measures the response via an off-diagonal component of the stress tensor, which is proportional to the momentum flux. In this case, the momentum flux is imposed, and the shear velocity profile is the system's response. We anticipate, the reverse NEMD method may not capture appropriately the deviations from the linear velocity profile during shear-thinning and shear-thickening regimes, in which case the direct perturbation algorithm will be used. Shear viscosities against shear rates will be plotted for all the state points, as well as variations of the normal stress differences with the time scale ratio between thermal fluctuations (short-term

motion of nano-particles, i.e. $d_{nn}/\sqrt{\langle v^2 \rangle}$ and the shear time $(1/\dot{\gamma})$, that is $d_{nn}\dot{\gamma}/\sqrt{\langle v^2 \rangle}$ where d_{nn} is the distance between nearest neighbor particles and v the relative velocity deviations from the linear profile imposed.

Pair radial distribution functions between nanoparticle centers' of mass will be computed to determine distribution effects and changes in viscosity. Mean square displacements (MSD) will also be computed to calculate nanoparticle diffusion (slope of MSD). We will dump velocities every 2fs in order to compute the velocity autocorrelations needed by the 2PT to calculate the changes in entropy and free energy of the system.