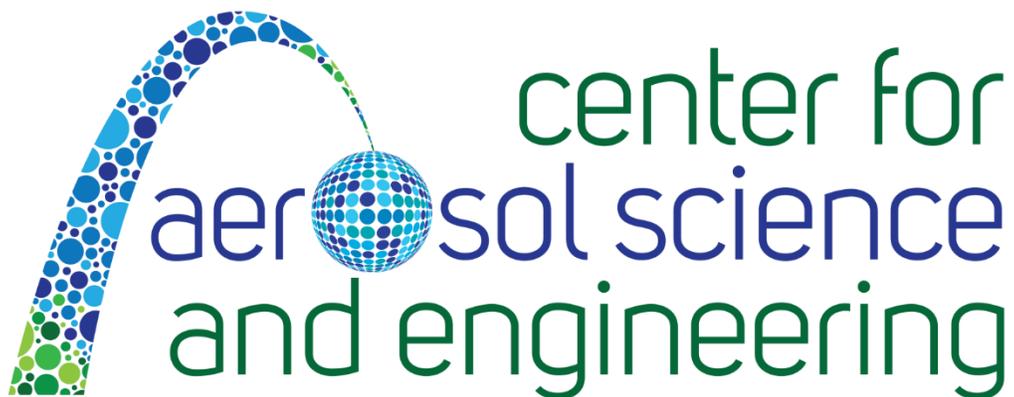# Abstract Booklet

1st Symposium on Nonequilibrium Multiphase Systems

Saint Louis, MO USA – December 7-8, 2018

Hosted at Washington University in Saint Louis (WUStL)

By the Center for Aerosol Science and Engineering (CASE)

Organizers: Elijah Thimsen (WUStL) and Chris Hogan (U. Minnesota)

Meeting Location:

Brauer Hall Room 12 (unless otherwise directed)
6220 Forest Park Parkway
Saint Louis, MO 63130, USA

Friday, 7th December
08:00 – Continental Breakfast
08:15 – Opening Remarks

Session I
Flame & Laser Systems
08:30 – Mark Swihart, SUNY Buffalo
09:00 – Angela Violi, Univ. Michigan
09:30 – Takafumi Seto, Kanazawa Univ.
10:00 – Rich Axelbaum, Washington Univ.

10:30 – Break

11:00 – **Keynote:** Mike Gordon, UCSB
      (Whitaker Hall Rm. 100)
12:00 – Lunch (Brauer lobby)

Session II
Plasma Systems
13:00 – Davide Mariotti, Ulster Univ.
13:30 – Peter Bruggeman, Univ. Minnesota
14:00 – Elijah Thimsen, Washington Univ.
14:30 – Vlad Vekselman, Princeton Plasma
      Lab
15:00 – Jan Benedikt, Kiel Univ.

15:30 – Break
15:45 – Breakout I (Brauer 3015 and 12)
16:30 – Poster show (2nd floor Brauer) and
      Tour of CASE facilities (3rd floor
      Brauer)
18:15 Adjourn
Evening – dinner in self-organized groups.

Saturday, 8th December
07:45 – Continental Breakfast

Session III
Particle Laden Systems
08:00 – Barbara Wyslouzil, Ohio State Univ.
08:30 – Lorenzo Mangolini, UC Riverside
09:00 – Anthony Beris, Univ. Delaware
09:30 – Christopher Hogan, Univ. Minnesota

10:00 – Break

Session IV
Transport Theory & Modeling
10:10 – Ranganathan Gopalakrishnan, Univ.
      Memphis
10:40 – Hai Wang, Stanford Univ.
11:10 – Carlos Larriba, IUPUI
11:40 – Dibyendu Mukherjee, Univ.
      Tennessee

12:10 – Lunch (Brauer lobby)

13:00 – Breakout II (Brauer 3015 and Brauer
      12)
13:45 – Summarize
14:00 – Adjourn

Laser- and flame-based synthesis of non-oxide nanoparticles

Mark T. Swihart

Chemical and Biological Engineering, University at Buffalo (SUNY), Buffalo, NY 14260

This presentation will provide an overview of two methods used in our laboratory for synthesis of non-oxide nanoparticles in the gas phase: laser pyrolysis and a flame-based method we call the high-temperature reducing jet (HTRJ) process. Both are examples of non-equilibrium multiphase systems that have proven to be powerful tools for preparing nanoparticles of materials that are not otherwise readily prepared, including metastable materials. However, our efforts to model these reactors have, to date, met with limited success. In laser pyrolysis, an infrared (10.6 micron wavelength CO_2) laser is used to rapidly and selectively heat vapor-phase precursors to initiate their decomposition and drive particle nucleation. In our implementation, the main reaction zone has a volume well below 1 cm^3, and this has greatly limited our ability to make meaningful *in situ* measurements. Modeling has provided some valuable insights, but direct comparisons of model and experiment have not yet been possible. Current efforts involve using liquid droplets as precursors, which introduces additional processes of laser-droplet interactions and droplet evaporation. In the HTRJ process, a fuel-rich hydrogen flame impinges on a converging-diverging nozzle that accelerates the hot combustion products to sonic or supersonic velocity. An aqueous solution of metal salts is injected into the throat of the nozzle, where it is dispersed into fine droplets that rapidly evaporate. Precursors decompose, and particles nucleate from the gas phase. Excess hydrogen ensures that metals that can be reduced by hydrogen in the presence of water (e.g. copper, silver, palladium, nickel, and their alloys) are produced as metals and not metal oxides. This is similar to flame spray pyrolysis, except that the combustion zone and particle formation zone are separated by the converging-diverging nozzle. Modeling of this process would require combining models for compressible flow, droplet generation, droplet evaporation, precursor decomposition, particle nucleation, and aerosol dynamics. This presentation will provide an overview of these two methods, their differences and commonalities, our attempts to date to model them, and the challenges that still limit our fundamental understanding of these processes.

Thermodynamics and kinetics during particle formation in combustion

<u>Angela Violi</u>

Departments of Mechanical Engineering, Chemical Engineering and Biophysics
University of Michigan

Reactive systems are ubiquitous in nature and have attracted great attention in theoretical, experimental and numerical fields. An example of such systems is combustion that is if great importance to the development of society, not only in terms of energy released by fuels, transportation but also for the synthesis of new materials. However, it is a challenge for traditional macroscopic or microscopic models to efficiently and accurately describe combustion phenomena where the span of spatial-temporal scales is relatively large and nonequilibrium phenomena play essential roles.

In this work, we report on the analysis of the mechanisms of formation of nanoparticles incombustion. In addition to the thermodynamic criteria for spontaneous processes, these environments present kinetic barriers that can intercept equilibration and preserve highly-ordered, high-energy non-equilibrium states. Molecular simulations are used to investigate the relative importance of thermodynamics and kinetics during the transition from small gas-phase species to macromolecular structures that can further grow into soot nuclei. This highly reactive region is characterized high temperatures (e.g., 1700K), large concentrations of radical species with phenomena happening on a very short time-scale (e.g., ps). This study highlights the need for a comprehensive approach that include free energy analysis, to understand the fundamental mechanisms that drive these processes.

Formation and growth of nanoparticles and nanomaterials by laser-induced high energy processes

Takafumi Seto, Tomoya Tamadate, Mohamed Abd El-Aal and Hidenori Higashi

Kanazawa University

Pulsed Laser Ablation (PLA) is a nonequilibrium multiphase process that generate nanomaterials by nucleation and growth of laser-vaporized species through the interactions with background species (gas, liquid and supercritical fluids). The extremely rapid quenching of vapor is advantageous in producing nanoparticles in the quantum size range (<10 nm). PLA is also applicable to synthesize various kinds of non-equilibrium materials such as nanocarbons and semiconductor nanowires. Nucleation of the laser-ablated species takes place at the interface between laser-induced plasma plume and background species. Therefore, it is important to analyze and control the dynamics of laser plume. Pressure, temperature, and phase of the working fluid have significant effects on the plume dynamics, which induces the drastic change in the size distribution and morphology of products. For example, silicon quantum dots can be generated by the PLA under the low pressure background gas (typically 300 to 1000 Pa). Crystal structure of the quantum dots can be improved by post or in-situ annealing process. In-situ annealing (laser oven process) has also advantages for activating small amount of catalytic elements, e.g., metals, to produce carbon allotropes (carbon nanotubes) and silicon nanowires by vapor-liquid-solid (VLS) mechanism. In general, increase in the background pressure has a negative effect that reduces the size of laser plume, and decrease the yield of nanoparticles because of the energy loss to the fluid. On the other hands, laser ablation in liquid has been widely used to synthesize nanocolloid suspension in a single step batch process. Our recent study on the PLA of graphite target in the low pressure gas, liquid and high pressure (supercritical) fluids showed variety of products such as nanoaggregates, onion-like carbon, and diamond-like carbon depending on the background gas density. More interestingly, multiple laser irradiation to the products may also induce phase transition of the products. Fabrication of the monodisperse nanoparticles and hybrid nanostructures by the advanced PLA process will be also presented.

I: Flame & Laser Systems

Understanding and perturbing structure within the high-temperature and composition gradients of non-premixed flames

Richard L. Axelbaum,[1] Scott A. Skeen[2] and Ben Kumfer[1]

[1]*Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130*

[2]*Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551*

Non-premixed flames consist of fast chemical reactions occurring within a region that is dominated by high gradients in temperature and composition. The relationship between the species, temperature and reaction rate profiles is dictated by the boundary conditions (i.e, oxygen and fuel concentrations. or, more fundamentally, the stoichiometric mixture fraction), which in turn affect various phenomena within the flame. This understanding of how boundary conditions affect flame structure under high gradients can be applied to interpret or control many unusual flame phenomena. For example, through understanding the interplay between the various profiles, the local chemistry can be affected to dramatically affect particle nucleation rates in flames. Complete suppression of soot formation can be achieved even at very high flame temperatures. Furthermore, other flame phenomena, such as flame strength (scalar dissipation rate at extinction) and the amount of oxygen at the location of peak temperature, can be strongly perturbed. Flames can be tuned to be highly resistant to extinction, having extinction scalar dissipation rates over 20 times greater than those of typical fuel-air flames with the same flame temperature. In this talk, the novel structure of these flames is described and the results interpreted based on flame structure and chemical kinetics. The coupling between heat and mass transfer, under nearly unity Lewis number conditions, allows for convenient interpretation of these phenomena. Various applications of this process are briefly described, including synthesis of high-purity single-walled carbon nanotubes and oxy-combustion for carbon capture and storage (CCS). Laser induced breakdown spectroscopy is shown to be a useful diagnostic tool to assist in interpreting flame structure.

Microplasma jet spray deposition of nanostructured materials

Michael Gordon

Department of Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106

The ability to synthesize a wide range of nanostructured materials, as well as integrate them into larger systems, is fundamental to the development of next-generation micro- and optoelectronic devices, sensors, and energy harvesting and storage technologies. Toward this goal, we have developed a versatile, plasma spray-like deposition technique, based on flow-through hollow cathode discharges at 10-100 Torr (microplasma jets), that can deposit nanoparticles, dense layers, and structured thin films of crystalline materials on virtually any surface (e.g., conductors, insulators, polymers, fibers, and lithographic patterns). Both supersonic and pressure-matched microplasma jets are seeded with organometallic precursors under reducing or oxidizing conditions to create a directed flux of growth species (e.g., atoms, ions, clusters, and/or nanoparticles) that are subsequently 'spray-deposited' onto the surface of interest at room temperature. A diverse range of nanostructured materials, e.g., metals (Cu, Ni, Pd), oxides (CuO, ZnO, MnO_2, RuO_2, NiO, Fe_2O_3, Co_xO_y), doped oxides ($Fe_xNi_{1-x}O$), and spinels ($NiFe_2O_4$), with different morphologies (nanoparticles, dense columnar films, or hierarchical nanostructures, etc.) can be realized with the technique. The talk will highlight material deposits formed in different flow regimes as well as T_{rot}, T_{vib}, T_e, and e^- density measurements on various jets made using trace gas OES and Langmuir probe studies.

Understanding fundamental mechanisms that are driving nanoparticle synthesis in atmospheric pressure plasmas

Davide Mariotti

Ulster University, NIBEC, Shore Road, Newtownabbey, BT37 0QB, UK

Synthesis of nanoparticles by plasmas is inherently a complex and dynamic multiphase approach. Plasma synthesis represents a unique method to deliver a range of nanoparticles with diverse compositions, sizes and surface characteristics, which are often unachievable with other synthetic techniques [1-7]. For these reasons, plasma processes can be used to propose and investigate novel and unique nanoparticles for a variety of applications therefore contributing to advance our understanding of materials at the nanoscale and beyond [3, 5, 8].

However the understanding of such multiphase plasmas has been lagging behind the success in delivering desired materials and materials properties. This is particularly true for atmospheric pressure plasmas due to a number of reasons that include complications in diagnostics and the relatively younger age of the research field. In this contribution a few case studies of nanoparticle synthesis will be discussed where a timid attempt will be made to shed some light on the formation mechanisms. Synthesis of nanoparticles from a few different precursors (gas, liquid, solid) will be presented and discussed. The case studies will also include, briefly, the discussion of some relevant processes taking place at the interface between plasmas and liquids that may be considered simplified/scaled-up configurations of some types of multiphase plasmas [9, 10].

These case studies will also give the opportunity to consider any similarities in the context of multiphase plasmas as well as identify challenges and opportunities that can be derived from a better understanding of the fundamental mechanisms.

1. *Askari S, Mariotti D, Stehr JE, Benedikt J, Keraudy J, Helmersson U Nano Letters 18 (2018) 5681*
2. *Ni C, Carolan D, Rocks C, Hui J, Fang Z, Mariotti D et al. Green Chemistry 20 (2018) 2101*
3. *Carolan D, Rocks C, Babu Padmanaban D, Mariotti D et al. Sustainable Energy Fuels 1 (2017) 1611*
4. *Maguire P, Rutherford D, Macias-Montero M, Mahony C Mariotti D et al. Nano Letters 17 (2017) 1336*
5. *Askari S, Haq AU, Macias-Montero M, Levchenko I, Yu F, Mariotti D et al. Nanoscale 8 (2016) 17141*
6. *Askari S, Švrček V, Maguire P, Mariotti D Advanced Materials 27 (2015) 8011*
7. *Askari S, Macias-Montero M, Mariotti D et al. Journal of Physics D: Applied Physics 48 (2015) 314002*
8. *Zhang R-C, Sun D, Lu A, Askari S, Mariotti D et al. ACS Applied Materials & Interfaces 8 (2016) 13567*
9. *Mariotti D, Belmonte T, Benedikt J et al. Plasma Processes and Polymers 13 (2016) 70*
10. *McKenna J, Patel J, Mariotti D et al. The European Physical Journal-Applied Physics 56 (2011) 24020*

II: Plasma Systems
Non-equilibrium aspects of plasma-droplet interactions

Gaurav Nayak and <u>Peter Bruggeman</u>

Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455

The interaction of atmospheric pressure plasmas with liquid droplets is a complex multiphase non-equilibrium phenomenon. While both gas and liquid phase chemistry have been studied separately in considerable detail, quantitative studies directly linking gas phase with liquid phase reactivity have been limited to modeling and lack experimental validation. We developed an experimental setup to study plasma-droplet interactions in a controlled and well reproducible environment. The setup consists of a diffuse glow discharge with a bulk uniform density of reactive species. A gas flow guides individual liquid micro-droplets produced by an on-demand droplet system through the plasma. This system enables the measurement of the gas phase reactive species densities, tracking droplet trajectories and evaporation and ex situ analysis of the collected droplets after plasma treatment. We will show preliminary results of the system that quantify non-equilibrium aspects of the system related to evaporation, droplet dynamics and the reactive chemistry in the context of the conversion of a model hydrocarbon compound in water.

State variables for nonequilibrium plasma process control

Elijah Thimsen

Energy, Environmental and Chemical Engineering, Washington University in Saint Louis, Saint Louis, MO 63130

Low temperature plasmas (LTPs) are open driven systems in which species have temperatures that may differ by more than an order of magnitude at the same macroscopic location in space. For example, electrons can have a temperature in the range from 10,000 to 100,000 K while the neutral molecules are near room temperature. For the prediction of LTP process outcomes, it is often ineffective to make the conventional assumption that the system will evolve towards the local equilibrium state. Examples of LTP processes proceeding away from the local equilibrium state from our work include 1) the evolution of an aerosol size distribution to decrease its geometric standard deviation, 2) the splitting of CO_2 at a neutral gas temperature and pressure where it is the dominant chemical spices in the carbon-oxygen system, and 3) a highly localized, very negative electrochemical potential of electrons in water that is in contact with LTP. Our hypothesis is that processes occurring in the bulk of the LTP, and at interfaces, evolve towards a *superlocal* equilibrium state that is defined by at least two new state variables in addition to the canonical variables T, P and $\{x_i\}$. Specifically, the two new state variables are electron temperature T_e and plasma density n. Evidence will be presented for the CO_2 splitting reaction that when the state variables are held constant, the CO_2 conversion increases with space time and then saturates at a steady state value. Moreover, the steady state conversion increases with n as T_e is held constant. The observations are consistent with the idea that the system is evolving towards a *superlocal* equilibrium state. The proposal is that robust LTP process control can only be achieved by actively measuring the plasma state variables and using feedback controls to maintain them within a well-defined range. Reliable methods to measure and control T_e and n in complex reactive LTPs is of paramount importance from this perspective.

Coagulation growth kinetics of nanoparticles in non-stationary plasma

Vlad Vekselman,[1] Yevgeny Raitses,[1] and Mikhail Shneider[2]

[1]*Princeton Plasma Physics Laboratory*

[2]*Princeton University*

Coagulation growth kinetics of nanoparticles in plasma is affected by inter-particle electrostatic forces due to charging phenomenon. In stationary plasmas, flux of plasma electrons reaching nanoparticles usually dominates over other charge carriers and particles acquire the so-called floating potential. Unipolar charging of particles results in retardation of nanoparticles growth and may result in limitation on a particle size. In current work we demonstrate opposite effect that is an enhancement of the particles growth in atmospheric pressure non-stationary arc discharge. Modeling of the growth kinetics revealed the formation of bipolar charge distribution of nanoparticles. As a result, Coulomb forces reversal from repulsive to attractive between nanoparticles promotes enhanced growth rates. This mechanism may explain an experimental observation of the grow of large micron size particles in the carbon arc.

Non-equilibrium plasmas in the plasma-surface interactions

Jan Benedikt[1], Beatrix Biskup[2], Mohamed Mokhtar Hefny[2], Christian Maszl[2], Sadegh Askari[1], Judith Golda[1]

[1]Faculty of Mathematics and Natural Sciences, Christian-Albrecht-Universität zu Kiel, 24098 Kiel, Germany

[2]Faculty of Physics and Astronomy, Ruhr-University Bochum, 44 780 Bochum, Germany

Low-temperature plasmas can provide highly non-equilibrium reactive environment, in which selectively heated electrons drive ionization, excitation, and in molecular gases also dissociation processes, whereas the gas temperature stays low. These conditions can be realized under low-pressure as well as atmospheric pressure conditions and provide many advantages such as well-known directional ion bombardment utilized in directional chemical sputtering or generation of reactive species for deposition of thin films. Our research focuses on the diagnostics of reactive low-pressure and atmospheric plasma-interaction with surfaces with focus on the role of individual plasma components such as ions, metastables, energetic photons, and radicals, and on their possible synergistic effects. Three examples will be presented, which illustrates the unique plasma properties. First, the analysis of ion effects in low-pressure inductively coupled plasma treatment and high-power impulse magnetron sputtering process will be discusses. An ion repelling grid system has been designed and used in both cases to suppress the ion flux to the surface. Second example will discuss the role of metastables in the surface chemistry during the growth of thin films under atmospheric pressure conditions. We have demonstrated that the flux of excited argon or nitrogen metastables can replace the surface oxidation in the growth process of SiO_2-like films from hexamethyldisiloxane (HMDSO) precursor. Moreover, the oxygen free gas mixture has even led to improved film properties. Third case will highlight the chemical non-equilibrium, which can be generated by cold atmospheric plasmas in aqueous solutions. Cold atmospheric plasma generated in dry gas mixture of helium with O_2 molecules is an effective source of oxygen atoms, which are effectively transferred into the aqueous solutions. This is a unique situation, because reactive processes in water or water vapor leads preferentially to the formation of OH radicals with another reaction pathways.

<center>**III: Particle Laden Systems**</center>

Heterogeneous nucleation in supersonic flow

Barbara E. Wyslouzil and Yensil Park

Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH 43210

Understanding condensation in high speed flows – whether it is initiated by homogeneous or heterogeneous nucleation – is critical in a broad range of engineering applications. These range from energy extraction from low-pressure steam turbines, dehydration and heavy hydrocarbon removal from natural gas, and the production of high speed nano-sized particles for cleaning surfaces, to the development of hypersonic wind tunnels. In some cases, particle formation and growth is the desired result, in others it is not. Furthermore, the outcomes depend strongly on whether the phase transition is initiated by homogeneous or heterogeneous nucleation. In either case, measuring the conditions required to initiate nucleation, the rates at which particles grow, and the size and structure of the final droplets are all crucial for developing accurate models of industrial processes.

Although supersonic nozzles have been used extensively for homogeneous nucleation studies, very little work has been done to understand heterogeneous nucleation in these devices. In part, this is because heterogeneous nucleation does not compete effectively with homogeneous nucleation until the pre-existing aerosol number density is on the order of 10^7 cm^{-3}. This talk will summarize our efforts to characterize heterogeneous nucleation under the highly non-equilibrium conditions characteristic of supersonic nozzle flow. To do so we produce the seed particles by homogeneous nucleation at higher temperatures and conduct the heterogeneous nucleation experiments by condensing a second species at lower temperature. The rich data set includes static pressure measurements to pinpoint the onset of homogeneous and heterogeneous nucleation, small angle X-ray scattering measurements to characterize the size and number density of the aerosol, and Infrared Spectroscopy to follow the state of each species. This talk will summarize our experimental results for heterogeneous nucleation of CO_2 onto water ice and n-alkane particles that were motivated by the possibility of using supersonic separators to capture CO_2 from flue gas.

III: Particle Laden Systems
Charging and heating of nanoparticles in non-thermal plasmas

Lorenzo Mangolini

Department of Mechanical Engineering, University of California Riverside, Riverside, CA 92521

Several theoretical contributions have predicted that dust immersed in a low-temperature plasma acquires a negative charge. Nanoparticle heating to temperatures that exceed those of the background gas is closely intertwined with charging effects, since it is largely due to the recombination of charged species at the nanoparticle surfaces. These phenomena are a direct consequence of the lack of thermal equilibrium between heavy species (close or slightly above room temperature) and electrons (few eV in temperature). In this talk, we'll summarize our ongoing effort to experimentally determine nanoparticle charge and temperature in low-temperature plasmas. A variety of techniques are used and developed for this purpose. For instance, a Langmuir probe is used to measure the deficit between ion and electron densities in a low-pressure dusty plasma. This corresponds to the charge carried by the particles dispersed in the plasma. *In-situ* FTIR is used to monitor the surface termination of nanoparticles in plasma. Thermally-induced desorption of surface species can be utilized as an indirect indicator of nanoparticle heating. These non-equilibrium effects enable the processing of materials that are difficult or impossible to process using other techniques. As an example, we will discuss the use of non-thermal plasmas for the development of a novel photocatalyst based on titanium nitride.

Applications of conformation tensor-based macroscopic models to particulate and multiphase flows

Antony N. Beris, Paul M. Mwasame and Norman J. Wagner

Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716

Particulate and multiphase flows are common in numerous industrial processes justifying the large amount of research dedicated to their study. Still most of their theoretical treatment relies on microscopic models that, albeit sophisticated enough to represent the often-encountered complex flow behavior, they have the inconvenience of requiring considerable computational resources and/or rather limited applicability to simple flow geometries. At the other extreme lie phenomenological continuum models that albeit easy to work with they do involve several adjustable parameters requiring many experiments to fit them and implying limited applicability to the range covered by those experiments. We propose here an intermediate approach, still at the continuum macroscopic level, but relying on structural-parameter based fluid model descriptions applied through a nonequilibrium thermodynamics-based approach. At that macroscopic level of description, a conformation tensor, **C,** is commonly used to represent the microstructure that characterizes the morphology of multiphase systems. For example, in dilute emulsions with droplet morphology, the dynamics of droplets can be simply represented through a contravariant conformation tensor of constant determinant, det(**C**)=1 [Maffetone Minale (1998)]. Such models have been previously postulated by various authors e.g. Maffetone Minale (1998) and Wetzel and Tucker (2001).

Recently, the Maffetone-Minale model has been recast and extended for arbitrary viscosity ratios (between the dispersed and the continuum phases) using the non-equilibrium thermodynamics bracket framework of Beris & Edwards (1994) [Massame et al., 2017]. In that work all the model parameters have been obtained through comparison to available asymptotic analysis results from the literature. Moreover, a further advantage of the bracket formalism, is that it most recently naturally led to a generalization of the dilute emulsion model under conditions under which particle inertia effects are important [Mwasame et al., 2018]. Again, all the model parameters have been obtained based on comparisons against previous asymptotic microscopic theory results [Raja et al. (2010)]. In this way, for the first time, one is able to macroscopically predict unique signature rheological features of emulsions seen only in the presence of particle (micro) inertia, such as negative first normal stress differences and positive second normal stress differences, as for example revealed by the microscopic simulations of Li and Sarkar (2005).

In the present work we offer two additional extensions of the conformation tensor-based multiphase modeling. In the first one, we describe how a two conformation tensors-based model

can describe the rheology of emulsions in the presence of Ostwald ripening. The resultant model allows for effective mass transfer effects to be systematically incorporated into the emulsion multiphase model. We are thus able the describe a population of droplets and their evolution in time along with the evolution of the rheology. In the second application, a model for the rheology of concentrated non-Brownian suspensions is presented following previous work of Phan-Thien (1995). Similar to Phan-Thien (1995), the microstructure in a concentrated suspension is represented through a conformation tensor that represents now the second moment of the unit vector along the center to center line connecting two generic spheres. However, unlike that work, the thermodynamically-based model formulated here following an extension of the bracket approach of [Beris and Edwards, 1994] is consistent with all viscometric functions in non-Brownian suspensions. In shear flows, the model predicts negative first and second normal stress differences that have been observed both experimentally and in simulation studies. These are accompanied by microstructure orientation and localization along the compressional axis of the shear flow field. Those two new applications of conformation-based theories to particulate/multiphase flows show the potential benefit drawn from the systematic, nonequilibrium thermodynamics-based approach followed here that may therefore prove useful to other future applications as well.

Acknowledgment

References

Beris, A.N. and Edwards, B.J., 1994. Thermodynamics of flowing systems: with internal microstructure.

Li, X. and Sarkar, K., 2005. Effects of inertia on the rheology of a dilute emulsion of drops in shear. Journal of Rheology, 49(6), pp.1377-1394.

Maffettone, P.L. and Minale, M., 1998. Equation of change for ellipsoidal drops in viscous flow. Journal of Non-Newtonian Fluid Mechanics, 78(2), pp.227-241.

Mwasame, P.M., Wagner, N.J., Beris, A.N. 2017. On the macroscopic modeling of dilute emulsions under flow. Journal of Fluid Mechanics, 831, 433-473.

Mwasame, P.M., Wagner N.J., Beris, A.N., 2018. On the macroscopic modeling of dilute emulsions under flow in the presence of particle inertia. Physics of Fluids, 30: 030704.

Phan‑Thien, N., 1995. Constitutive equation for concentrated suspensions in Newtonian liquids. Journal of Rheology, 39(4), pp.679-695.

Raja, R.V., Subramanian, G. and Koch, D.L., 2010. Inertial effects on the rheology of a dilute emulsion. Journal of Fluid Mechanics, 646, pp.255-296.

Wetzel , E. D. & Tucker R III, C. L. 2001 Droplet deformation in dispersions with unequal viscosities and zero interfacial tension. J. Fluid Mech. **426**, 199-228.

Kinetic energy transfer influences on particle growth rates and transport in non-equilibrium aerosol systems

Christopher J. Hogan, Chenxi Li, & Huan Yang

Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455

Non-Equilibrium aerosols can be defined as systems wherein the translational kinetic energies or the internal energies (i.e. temperatures) of the suspended particles differ significantly from that of the surrounding gas. Such situations are encountered when particles are accelerated to supersonic or hypersonic speeds followed by deceleration of the gas, when particle nucleation and collisional growth rates approach the particle-bath gas collision rate (high concentration, growing systems), and in dusty plasmas. In large part, particle transport and growth rates in such systems have not been studied; in the case of high speed particles the drag coefficient in the Mach and Knudsen number dependent regime has not been fully described, and in high concentration and plasma systems assumptions of fast equilibration between particles and the gas are made almost universally. This presentation will highlight our group's efforts to develop theoretical and numerical approaches to understand particle transport and growth in non-equilibrium aerosols. Two case studies will specifically be discussed: (1) the migration of particles at supersonic speeds through a shock front (encountered in aerosol deposition based manufacturing) and (2) the effects of elevated particle/cluster internal energy on condensational growth.

Langevin dynamics modeling of gas-phase ion-ion recombination rates

Harjindar Singh Chahl and Ranganathan Gopalakrishnan

The University of Memphis, Memphis, TN 38152

Ion-ion recombination/neutralization reactions are an important step in the chemical dynamics of flames, plasmas, planetary atmospheres, inter-planetary gas disks and many other ionized gas environments. In-spite of a plethora of experimental data available for positive ion-negative ion recombination rates in various background gases, the role played by background gas molecules that lead to ternary interactions of the form $A^+ + B^- + X \rightarrow AB + X$ (X represents a neutral gas molecule) remains unclear. The kinetic energies of the colliding species A^+ and B^- are increased due to their long range ~r^{-1} Coulombic attraction and are thus driven out of thermal equilibrium in their approach towards each other (r is the radial distance between the ions). The ion-ion recombination rate is determined by the diffusion-limited transport of the colliding species A^+ and B^- and a distance dependent probability of electron tunneling. Depending on the electron affinities of the colliding ions, the distance at which an electron has a high probability of tunneling across to complete the neutralization may vary but generally, it is estimated to be ~10 angstroms. The ion-ion separation distance constantly fluctuates due to the competition between the short range (~r^{-6}) dipole attraction forces, very short range (~r^{-12}) repulsion and collisions with neutral background gas molecules. In this investigation, a Langevin Dynamics approach is undertaken to simulate the ion-ion "collision" in the presence of a background gas that acts as a thermal bath. Langevin Dynamics offers a computationally inexpensive approach to calculating the collision rate as well as the non-equilibrium ion velocity distribution function due to acceleration. "Collision" is restricted to the approach of ions, without considering electron tunneling here. Depending on the chemical nature of A^+ and B^-, a complex potential based on density functional theory calculations may be selected to model specific ion pairs. Here, the colliding ions A^+ and B^- are modeled to interact through a potential that comprises of 1) a long range Coulombic attraction ~r^{-1} that arises due to their charge, 2) a short-range van der Waals attraction ~r^{-6} that arises due to dipole-dipole interactions parameterized by their observed/calculated permanent dipole moments, and 3) a very short range repulsion interaction that is presumed to arise from electron degeneracy pressure and is widely assumed to be of the order of ~r^{-12}. These generic potentials are chosen to capture the distribution of ion-ion spacing and kinetic energy, and the dependence of the transport rate (of species A^+ and B^- towards each other) on the measurable properties of the ions (mass, low-field electrical mobility, dipole moment per unit volume) and the gas (temperature and pressure). Scaling analysis of Langevin trajectories of ions is carried out to describe gas-phase ion-ion recombination. Parameterization of the diffusion-limited transport rate as a function of experimentally measurable ion and gas parameters will be presented to develop rigorous physics-based models to possibly re-analyze and interpret published recombination rates.

Nanoparticles in dilute gases: fundamental equivalence between momentum accommodation and surface adsorption

Hai Wang and Changran Liu,

Stanford University, Stanford, CA 94305

We demonstrate the fundamental equivalence of momentum accommodation of nanoparticles in dilute gas and surface adsorption of the gas on nanoparticle surfaces. Momentum accommodation is a key factor governing particle transport properties including electric mobility, Brownian diffusion, and the various phoretic properties (e.g., thermophoresis). It is known that momentum accommodation is related to two distinctive outcomes of gas-particle collisions, namely diffuse reflection and specular reflection. A transition from a diffuse-reflection to specular elastic reflection occurs as the size of the particle approaches the molecular or cluster size of a few nanometers in diameter. In this work, the relationship between momentum accommodation and surface adsorption is studied in detail. Molecular dynamic simulations show that surface adsorption is the key mechanism behind diffuse scattering; and that the immediate reflection and surface adsorption events are governed by the kinetic energy distribution of rebounding gas molecules upon collision with the particle surface. Furthermore, the momentum accommodation factor is shown to be equal to to the probability of surface adsorption. The kinetics and equilibrium of physisorption are examined to shed light on the effect of the lifetime of surface adsorbates on momentum transfer. A statistical treatment is proposed for the adsorption and hence, the gas-nanoparticle momentum accommodation coefficient. The validity of the treatment is tested by comparing the results against experimental mobility of silver nanoparticles in air.

Field dependent and orientation dependent mobility calculator with accommodation

Carlos Larriba-Andaluz and Tianyang Wu

Mechanical Engineering, Purdue School of Engineering and Technology, Indianapolis, IN 46202

The ability to predict the ion/electrical mobility of a charged entity from a molecular model is becoming of increasing interest as high resolution mobility measurements are more readily available. As such, we previously developed a very efficient parallelized state of the art suite of algorithms, IMoS, that calculates collision cross sections (CCS) and mobilities of ion, clusters and nanoparticles within the free molecular regime from all-atom structures or coarse grain models.

The existing algorithms in IMoS, however, have their limitations. Among such limitations, most relevant are that 1) calculations always assume that all orientations are equally probable, 2) the mobility is independent of the electric field (true for $E/N << 0$), 3) all atoms/coarse grained structures are assumed fixed which requires accommodation and reemission laws to be assumed and 4) the ion/nanocluster has no rotational velocity when the gas-ion momentum exchange occurs.

Here we propose a novel Molecular Dynamics/MonteCarlo algorithm that explores the drift-diffusion of an ion/nanoparticle as if it were in a real gas and subject to an arbitrary field in three dimensions. The ion/nanoparticle can freely rotate, and its orientation, angular velocity and drift velocity are a function of the gas/ion collisions, the reduced mass, the strength of the field, and the position of the charges within the ion. It is the effect of the collisions and the particle orientation together with the electric field that now establishes the equilibrium drift velocity, preferred orientation, if any, and angular velocity. This equilibrium drift velocity, together with non-linearized theory ultimately establishes the relation between field and mobility. The algorithm will not only provide new insights into mobility calculations in high fields and non-linear conditions but will also provide a unique understanding in multiple applications which involve charging efficiency, instrument sensitivity, diffusion losses, kinetic rates or even collisional heating (when coupled with MD). The algorithm may be parallelized and provides results within reasonable time. The code may also be extended out of the free molecular regime and into the transition regime when certain considerations are taken into account.

Kinetic Monte Carlo models to study the evolution of metal nanoparticles grown via homogeneous nucleation

Dibyendu Mukherjee

Department of Mechanical, Aerospace & Biomedical Engineering, Nano-BioMaterials Laboratory for Energy, Energetics & Environment (nbml-E3), University of Tennessee, Knoxville, TN 37996

Our group has pioneered a nanoparticle (NP) synthesis route interfacing laser ablation synthesis in solution with galvanic replacement reaction (tandem LASiS-GRR) techniques that allows disruptive merger of high-energy laser ablation with redox-driven chemical reactions to initiate non-equilibrium pathways for metal/intermetallic NP formations. Although such routes are promising to tune the physico-chemical properties of metal NPs, it requires a fundamental understanding of the thermodynamics and kinetics of the early-stage inception of metal NPs, a relatively ill-understood grand challenge problem that is largely driven by gas-phase homogeneous nucleation and growth inside the laser-induced cavitation bubble. Typically, gas-phase metal NP formations involve rapid cooling of supersaturated metal vapor (monomers) that leads to nucleation and birth of a stable critical cluster followed by the growth of the critical cluster via competing coagulation/coalescence processes and simultaneous interfacial reactions including surface oxidation. Experimental techniques to study such complex processes with diverse time scales is challenging. Hence, we present a series of hi-fidelity kinetic Monte Carlo models (KMC) as powerful tools for detailed mechanistic studies of these processes in an efficient and robust manner. The talk will start with gas-phase homogeneous nucleation modeling built on the Classical Nucleation Theory (CNT) of Gibbs' free energy-driven collisional processes (condensation/evaporation), and discuss the validity of steady-state nucleation rates. This will be followed by KMC-based studies on the non-linear interplay between competing non-isothermal coagulation-coalescence processes leading to surface oxidation and fractal-like morphologies of NPs grown in aerosol phase. Simulation results for Al NP case-study in air under different processing conditions (temperature, pressure, volume loading) show the efficacy of the model in determining optimal process variables for tuning structural and chemical make-up of metal NPs.

Poster Session

Soot formation models for non-premixed flames with variable stoichiometric mixture fraction and strain
Phillip Johnson, Rajan Chakrabarty, Ben Kumfer

Aerosol synthesis of metal-based nanomaterials in a flame-driven high temperature reducing jet reactor
Mohammad Moein Mohammadi, Shailesh Konda, Santosh Gunturi, Shikuan Shao, Raymond D. Buchner, Mark T. Swihart

Investigation of morphology and energetic characteristics of graphite-coated aluminum nanoparticles synthesized via laser ablation in organic solvents
Davari S.A., Gottfried J.L., Liu C., Ribeiro E.L., Duscher G., Mukherjee D

In-situ monitoring of nanoparticle generation in plasma
Oleksandr Polonskyi, Alexander Vahl, Jonas Drewes, Alexander Hinz, Thomas Strunskus and Franz Faupel

Application of real-time in situ diagnostics for characterization of plasma, gas phase composition and nanoparticles in atmospheric pressure arcs for synthesis of nanomaterials
Y. Raitses, V. Vekselman, S. Yatom, A. Gerakis, A. Khrabry, B. Stratton, M. Shneider and I. Kaganovich

Aerosol aerotaxy of III-V semiconductor nanocrystals in low temperature plasma
Necip B. Uner, Elijah Thimsen

Non-equilibrium aspects of plasma-droplet interaction
Gaurav Nayak and Peter J Bruggeman

Experimental study of how nanoparticles affect plasma properties in atmospheric-pressure dusty plasma systems
Nabiel Abuyazid, Chris Hogan and Mohan Sankaran

Online size distribution determination in low pressure plasma synthesis reactors
Xiaoshuang Chen, Takafumi Seto, Uwe R. Kortshagen, and Chris Hogan

On the limit of crystallization in a series of supercooled short-chain *n*-alkane nanodroplets
Kehinde E. Ogunronbi and Barbara E. Wyslouzil

Growth of molecular clusters to sub 10 nm particles: Kinetically controlled processes
Girish Sharma, Huang Zhang, Sukrant Dhawan, Yang Wang, Mengda Wang, Pratim Biswas

Molecular dynamics of ion and highly charged nanoparticles generated by electrospray
Tomoya Tamadate, Hidenori Higashi, Mikio Kumita, Yoshio Otani, and Takafumi Seto

Directory of Attendees

Abuyazid,	Nabiel	Case Western Reserve University
Axelbaum,	Richard	Washington University in St. Louis
Benedikt,	Jan	University of Kiel
Beris,	Antony	University of Delaware
Bruggeman,	Peter	University of Minnesota
Carbone,	Francesco	Yale University
Chahl,	Harjindar Singh	University of Memphis
Chen,	Xiaoshuang	University of Minnesota
Davari,	Seyyed Ali	University of California-Davis
Gopalakrishnan,	Ranganathan	University of Memphis
Gordon,	Mike	University of California-Santa Barbara
Hogan,	Chris	University of Minnesota
Kumfer,	Ben	Washington University in St. Louis
Larriba,	Carlos	Indiana University-Purdue University-Indiana
Maguire,	Paul	Ulster University
Mangolini,	Lorenzo	University of California-Riverside
Mariotti,	Davide	Ulster University
Mohammadmoein,	Mohammadi	University at Buffalo
Mukerjee,	Dibyendu	University of Tennessee-Knoxville
Nayak,	Gaurav	University of Minnesota
Ogunronbi,	Kehinde	Ohio State University
Polonskyi,	Oleksander	University of Kiel
Raitses,	Yevgeny	Princeton Plasma Physics Laboratory
Seto,	Takafumi	Kanazawa University
Sharma,	Girish	Washington University in St. Louis
Swihart,	Mark	University at Buffalo
Tamadate,	Tomoya	Kanazawa University
Thimsen,	Elijah	Washington University in St. Louis
Uner,	Necip B.	Washington University in St. Louis
Vekselman,	Vlad	Princeton Plasma Physics Laboratory
Violi,	Angela	University of Michigan
Wang,	Hai	Stanford University
Wyslouzil,	Barbara	Ohio State University