Science-based model for particle formation from novel fuels

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Abstract. With the advent of petascale high-performance computing platforms, realistic multiscale modeling can be constructed to incorporate atomic-scale (molecular) information into macroscopic predictions of engineering systems. The overriding theme of the work presented in this paper is developing a multiscale modeling approach for soot formulation where atomistic data is integrated into macroscopic simulations. The prediction of soot formation remains arguably one of the most challenging subjects in combustion science, having an influence over a wide range of applications ranging from combustion efficiency to reducing emissions to slow global warming, to improved heat transfer designs in industrial settings, to predicting the radiation heat transfer from large scale fires. Starting from the fuel structures the new multiscale simulations reveals how chemical changes and transformation can propagate upward in scale to help define the function of the particle structures. In particular, the fuel structure influences the morphology of the nanoparticles, which in turn is critical in determining the overall growth and agglomeration behavior. These simulations make use of a newly proposed combination of molecular dynamics and kinetic Monte Carlo methodologies that will include both chemical reactions and agglomeration processes. The main strength of this approach is the ability to use important atomic-scale information directly into large scale description of the macroscopic phenomena.

1. Introduction

Science and engineering have been revolutionized by the infusion of computational science and simulation in the traditional experimentation-observation-analysis-theory loop and by eliminating the geographic constraints for collaboration and experimentation. New means of computational discovery will augment the traditional discovery-innovation loop with novel computational concepts to aid knowledge discovery, analysis, and experimentation. Petascale computing will allow the prediction of complex system behaviors with unprecedented speed and accuracy. To capitalize on these advances and the enormous potential they hold, we require basic research into the scientific components of modeling and simulation.

The scope of this work is to gain an understanding of the complex phenomena occurring in systems composed of reactive carbonaceous nanoparticles, developing a new paradigm that couples the microscopic information about fuel structures with the description of particle formation (soot) from combustion sources.

The fundamental challenge in predicting soot formation lies in the fact that soot formation is a heterogeneous process at even atomic-length scales, ~$O(10^{-10}\text{m})$, which has an enormous impact on the soot morphology and overall yield. Recent work of Violi et al. [1, 2] has revealed how chemical changes

and transformation can propagate upward in scale to help define the function of the particle structures. In particular, the morphology of the nanoparticles is critical in determining the overall growth and agglomeration behavior. Current detailed soot-modeling approaches that have been developed for premixed [3-5] and nonpremixed flames [6, 7] do not account for key morphology dependent nucleation, surface growth, and agglomeration processes and may help explain current discrepancies between observed and predicted amounts of soot formed for even well controlled systems [5, 8, 9]. In addition, the models currently in the literature offer mathematical simplicity but do not yield chemical detail on the high molecular weight species. To help resolve issues such as identification of pathways leading to soot formation, we need to characterize the precursors, in terms of chemical structure andcomponents. Studying relationships between structure and pathways, structure and properties, and structure and reactivity (population of active sites) can lead to a deeper understanding of nanoparticle growth mechanisms. In current models, parameters related to structures are fitted to experimental data.

The new multiscale computational approach can describe the formation of particles following the evolution from fuel, gas-phase species into particles, preserving chemical and physical details of the compounds. The work presented in this paper is designed to help reveal, through multiscale computer simulation, how chemistry (chemical structures or changes at the scale of the molecular building blocks of nanoparticle agglomerates) will influence the emergent structure and function of particle assemblies at significantly large length and time scales. This can be achieved by providing a computational infrastructure to help connect the different scales of chemistry and physics. Carbonaceous nanoparticles will be characterized both chemically and physically, to study their formation and transformation mechanisms in combustion systems.

A major feature of this study is the identification of the chemical specificity of nanoparticles: size, chemical functionalities, and water solubility have a decisive role in establishing the interactions of aerosol with human tissues in the lungs. The same parameters establish their optical properties relevant to direct radiative forcing and to their ability to act as cloud condensation nuclei.

A timely application of this novel computation infrastructure is related to energy and transportation. The automotive industry is facing a challenging goal of further reducing fuel consumption and increasing performance while obtaining cleaner exhaust gas and greater driver comfort. Meeting the challenge of developing and optimizing the combustion processes of bio-diesel fuels in new engines will require a new level of the understanding of the physical and chemical phenomena common to diesel engines and low-temperature combustion engines, which will be strongly affected by the different fuel properties, which in turn affect fuel/air mixture preparation, combustion and emissions. Soot formation is one of the major constraints in engine performance.

After describing the methodology employed to compute chemical and physical properties of nanoparticles in different environments, we present a section on petascale computations and the need to develop a multiscale architecture to study the phenomena involved in soot formation such that the atomistic-level processes (chemistry) can be coupled with the very long length and time-scale processes.

2. Multiscale computational approach: the AMPI code

In high-temperature environments, particle formation from small gas-phase species is a fascinating multiscale problem of nanoparticle growth, both in length scale and in time scale. Starting from simple gas-phase molecules, such as ethylene and acetylene, polycyclic aromatic hydrocarbons including naphthalene and pyrene are formed. The system then undergoes a nucleation process, and the first particles are formed by reactions with the gas-phase species. Coagulation and agglomeration of these nanoparticles lead to particle size of the order of hundreds of nanometers in diameter [10]. The processes involved in the

formation of particles exhibit a wide range of time scale, spanning pico- or nanoseconds for intramolecular processes to milliseconds for intermolecular reactions.

For these systems, the coupling between scales can be very strong, and "bidirectional," and microscopic phenomena not only are driven by macroscopic forces but also change these macroscopic forces. In this case, there is a feedback loop between the microscopic and macroscopic scales. For example, particle clusters explicitly contain both micro- and macroscale dimensions in their structure, and the proper modeling of trans-temporal and trans-spatial structures involves crossing this microscopic/macroscopic barrier to incorporate an adequate degree of information transfer between these disparate scales [11]. Because of the small time-step required to integrate the equations of motion, molecular dynamics (MD) – the standard method for dynamical simulations at the atomistic level – is generally limited to nanoseconds. However, the relevant thermally activated processes typically take place over time scales of microseconds or even longer. Although MD simulations provide a powerful tool for investigating complex systems, their substantial computational costs limit their application to investigations on time scales that are less than microseconds and length scales that are significantly less than micrometers [12, 13].

The novel multiscale approach is embedded in the Atomistic Model for Particle Inception (AMPI) code, which combines the MD methodology with kinetic Monte Carlo to allow the extension of the accessible time scales by orders of magnitude relative to direct MD, while retaining full atomistic details of the systems of interest [14].

2.1 The Kinetic Monte Carlo method

Kinetic Monte Carlo (KMC) method is part of a broad class of algorithms that solve problems through the use of random numbers [15, 16]. It was developed for evolving systems dynamically from state to state [17]. The underlying principle in all KMC algorithms is the random selection of a process based on the transition probabilities of all processes, execution of the selected process, and updating the time clock and the transition probabilities [18].

The starting point for a stochastic description of a system is the underlying master equation given by [19]:

$$\frac{dP(\underline{\sigma})}{dt} = \sum_{\underline{\sigma}} G(\underline{\sigma}' \rightarrow \underline{\sigma}) P(\underline{\sigma}') - \sum_{\underline{\sigma}} G(\underline{\sigma} \rightarrow \underline{\sigma}') P(\underline{\sigma})$$

(1)

with $\underline{\sigma}' \neq \underline{\sigma}$, which gives the evolution of the probability density function $P(\underline{\sigma})$ of observing a state $\underline{\sigma}$, $G(\underline{\sigma} \rightarrow \underline{\sigma}')$ is an element of the transition matrix for the transition from state $\underline{\sigma}$ to state $\underline{\sigma}'$ [20]. Atoms or molecules vibrate around locations separated by large free energy barriers and occasionally jump from one location to a nearby one. The momentum degrees of freedom of all atoms and molecules and thermal vibrations are integrated out to compute the microscopic rates used in a stochastic description of a system. The resulting microscopic state variable $\underline{\sigma}$ is a function of only spatial and time coordinates. The atomic jump results in a change in $\underline{\sigma}$ once the jump has occurred. Recently Chatterjee and Vlachos have published a thorough overview of the kinetic Monte Carlo methods and we refer the reader to their paper [21] and citations therein for detailed information on the microscopic and accelerated KMC methodologies.

In summary, in the kinetic Monte Carlo method, the system starts in some state and equations of motion are never directly evolved, but a set of escape pathways connect a state to neighboring states. The key requirement is to specify these escape paths and the rate constant for each one. Given this set of rates, a

stochastic algorithm is employed to advance the time and to choose a neighboring state to which the system is moved. The rate constants for the possible moves out of each state are either computed by using first-principles calculations and transition state theory or determined by using the reaction class theory to make a rate catalog [13].

2.2 Molecular dynamics

In the broadest sense, molecular dynamics is concerned with molecular motion and conformational transitions together with local vibrations are the usual subjects of MD. Molecular dynamics alters the intramolecular degrees of freedom in a stepwise fashion, where the steps meaningfully represent the changes in atomic position over time (i.e., velocity) [20, 22]. Newton's equation is used in the molecular dynamics formalism to simulate atomic motion. The rate and direction of motion (velocity) are governed by the forces that the atoms of the system exert on each other as described by Newton's equation. Knowledge of the atomic forces and masses can then be used to solve for the positions of each atom along a series of extremely small time steps (on the order of femtoseconds = 10–15 seconds).

If the potential gives an accurate description of the atomic forces of the system, then the dynamical evolution will be an accurate representation of the real physical system. This explains the popularity of the MD method.

A serious limitation, however, is that accurate integration requires time steps short enough (~10–15 s) to resolve the atomic vibrations. The total simulation time is typically limited to less than one microsecond, while important processes such as diffusion, annihilation, nanoparticle assembly, often take place on much longer time scales.

To summarize, MD simulations follow the dynamical evolution of a system and generate a sequence of points in phase space as function of time corresponding to different conformations of the system and their momenta. This process requires choosing an interatomic potential for the atoms and a set of boundary conditions.

2.3 The AMPI code: synergy between KMC and MD

The AMPI code combines the strengths of KMC and MD methodologies in a unique way. The two modules are placed on an equal footing, and the code alternates between MD and KMC steps during the simulation. This feature represents the peculiarity of the new proposed methodology; the two approaches have been widely used [23] but never been integrated in this way. The novelty of this code lies in the synthesis of methods used to describe reacting systems over long time scales while retaining fully atomistic detail of the system itself.

The algorithm used in the AMPI code includes the following steps [14]:

1. The code reads a set of inputs, such as reaction rates for the KMC module and MD-related quantities.
2. It counts the number of sites available for reactions in the system by identifying each atom as belonging to a specific reaction class, and a rate catalog of possible reactions at a specific time t is constructed.
3. After classifying the reactions as either accepted or rejected, a KMC step is performed, and the structure of the growing species is modified according to the selected reaction. The clock is then incremented in a way that is consistent with the average time for escape from that state, which can be determined easily from the rate constants for the possible escape paths in the list.
4. The code relaxes the newly formed structure using a MD run, allowing for relaxation of the structure towards thermal equilibrium. The potential used to describe hydrocarbon interactions is the adaptive intermolecular reactive bond order (AIREBO) [24]. The potential describes the covalent bonding interactions largely as in Brenner's REBO potential [25].

At this point a new kMC step is performed, and the sequence of steps is repeated. Before performing the next kMC step, the global update method is used in order to re-evaluate all interparticle interactions and all process transition probabilities after a process is executed.
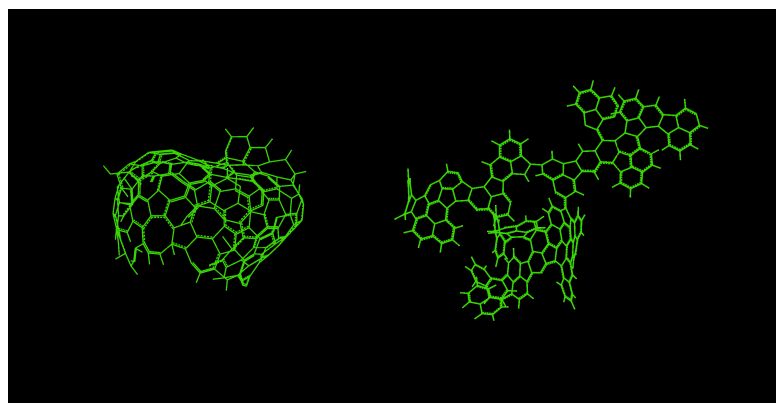
3. Results

The AMPI code is used to understand the physical and chemical processes involved in the formation of nanoparticles in different conditions of temperature, pressure and species concentrations starting from small aromatic compounds. The initial system, used in this example, is composed of 300 gas-phase species at 1500K and 1 atm. The goal is to understand how one of these species, for example benzene evolves into a three dimensional structure of thousands of atoms over long time scales. The three main modules are gas-phase species that can react with the growing species, reaction sites on the growing particle, and reaction rates. For the gas-phase input, the user defines the temperature and the concentrations of the species that contribute to the formation of the nanoparticles. Examples of common gas-phase species for the high-temperature environment are H, OH, H_2, and aliphatic and aromatic species C_xH_y with x and y varying from 1 to 24.

Once the species are defined, it is important to list the possible reactions that can occur over time and describe them in terms of reaction sites, that is, atoms where a particular reaction can occur. The reaction site module governs the definition and counting algorithm of reaction sites, which are capable of undergoing modification (for example, additional reactions). Examples of reaction sites included in the AMPI code are an tom on a 5- or 6-membered ring and an sp^3 carbon.

The third input to the AMPI code is the list of the rate constants that are extracted from smaller length and time scales simulation tools, such as density functional theory (DFT) [26-28], transition state methods, transition state theory (TST) [29], and molecular dynamics [30]. The reactions included in the AMPI code can be broadly classified into three categories.

The unique capability of AMPI code has been succesful in reproducing physical and chemical characteristics of nanoparticles in different environments [14, 31-36]. Nanoparticles have been characterized in terms of chemical structure/components and relationships between structure and pathways, structure and properties, and structure and reactivity population of active sites have been addressed. Results show the comparison between computed properties and experimental data in terms of H/C trends, particle morphology, depolarization ratio, and free radical concentration [2, 14, 19, 34, 35, 37].

The AMPI code also has been successful in identifying reaction mechanisms for the formation of nanoparticles. For example, the AMPI code can identify the role of accessibility to reaction sites on the relative rate of reactions of different molecules. During the site-counting procedure, the code identifies every atom with a local environment that fits the definition of each site listed as input to the code. At the same time, it also checks whether there is sufficient space next to the site for a gas-phase species to penetrate and react. In this way, an atom is considered as a possible site for termination or addition by a gas-

Example of nanoparticles of different morphology produced with the AMPI code.

phase species only if the gas-phase species of interest can be accommodated. The code goes over all atoms in the cluster, including all the possible sites, even the "hidden" ones that may be located inside the structure. The figure on the left shows particles produced from different combustion environments. It was found that the accessibility of the sites on the growing seed molecule decreases with increases in the curvature of the seed particle and size of the reacting molecule. This result can be used to identify new reaction mechanisms for the formation of nanoparticles of specified morphology.

For these systems, the presence of the MD module in the AMPI code is a determinant for a correct representation of the system. Rearrangements reactions are identified by MD leading to structural changes of the particle.

Besides growing by surface addition, the newly formed particles can grow by coalescence/coagulation to produce particles of 20–40 nm [1, 37, 38]. The figure below shows the influence of morphology on particle clustering. The right panel shows particles formed in an aromatic flame – total number of C=189 while the left side presents structures from an aliphatic flame (total number of C atoms is 214). The round particles, characteristic of benzene flames, tend to cluster and exhibit a preferred orientation with the open sections of the particles facing away form each other. The sheetlike particles produced in an acetylene flame, however, show a different behavior. They have more trouble getting together, and they tend to form stacking structures. These results demonstrate that the morphology of the nanoparticles is critical in determining the overall growth and agglomeration behavior.
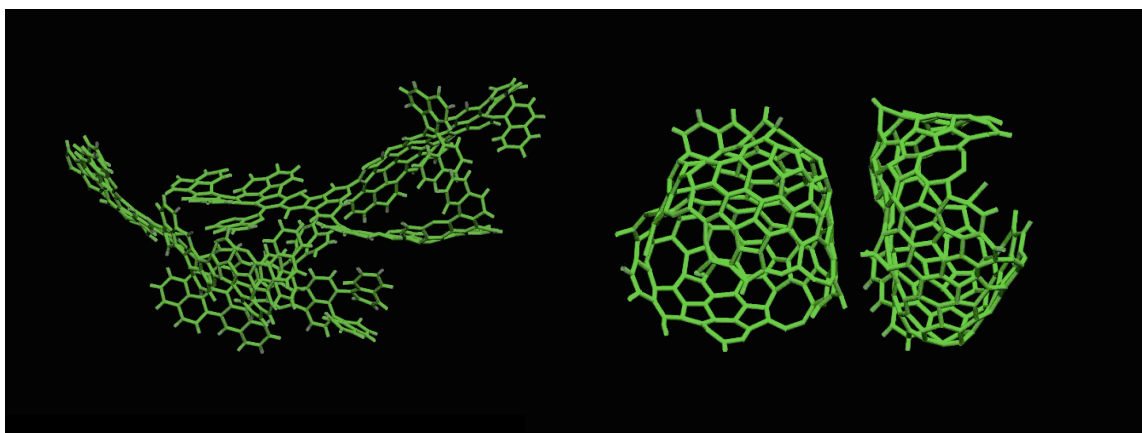
Particles from an aliphatic flame – left panel – and from an aromatic flame on the right. The clustering behavior of the two systems is different.

The replacement of petroleum-derived fuels by biofuels from renewable resources has gained worldwide interest and is scientifically investigated for its environmental costs and benefits [39]. The chemistry of these new fuels, however, is poorly characterized, particularly under conditions relevant to next generation engine designs. The trend of fuel diversification needs a comprehensive science foundation that must span a range of knowledge from the most fundamental facets of fuel chemical and physical properties to the impact of these properties on the aspects of the performance and emissions of the emerging new engine technologies. The multiscale approach presented in this paper makes it possible to bridge the chemical characteristics of new fuels including reaction pathways and new oxygenated species with the dynamics of particle formation and agglomeration to produce a unified description from

fuel properties, such as oxygen content, to particle characteristics, such as morphology and chemical composition.

4. Needs for petascale computing

The work reported in this paper describes a multiscale computational approach that makes it possible to correlate the structures of fuels with the morphology of nanoparticles that is critical in determining the overall growth and agglomeration behavior of higher molecular structures compounds (soot). Specifically, the method reveals how chemical changes and transformation can propagate upward in scale to help define the function of the particle structures. In particular, the morphology of the nanoparticles is critical in determining the overall growth and agglomeration behavior of higher molecular structures compounds (soot). The unique and powerful tool, embedded in the AMPI code, uses information on the chemistry occurring at the atomistic level and bridges it in a multiscale fashion to describe long timescale changes. The code combines the strengths of molecular dynamics and kinetic Monte Carlo and integrates them in a novel way. The synergy of the methods leads to a powerful computational approach that can describe the evolution of reactive systems over long time scales (seconds). To observe a statistically significant number of coagulation events, a large particle ensemble (10^6) has been shown to be effective [2].

With regard to the coagulation process, molecular dynamics simulations of systems composed of particles of different morphologies are used to understand the effect of shape and chemical composition on the clustering assemblies. Current levels of computing allow for roughly 10^4 nanoparticles to be formed using approximately 2×10^6 atoms over nanosecond time scales. These calculations currently take about 14 days running on 16 processors (where each processor is a circa 2006 commodity processor) using the GROMACS molecular dynamics package. At this level of simulation, soot precursor clusters of approximately 20nm can be formed and studied numerically. For realistic predictions of soot formation, soot clusters of size approaching 1μm are needed, resulting in a factor of 50 increase in computational requirements. Furthermore, the physical dimensions will also be increased accordingly, resulting in a factor of 125,000 more atoms, or roughly 10^{11} atoms in total. With coarse-graining approaches, the number of computational particles will naturally be fewer but will still be on the order of 10^7 nanoparticles. With petascale computing we could begin to approach these requirements.

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